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Abstract

In this article, we clarify the mathematical framework underlying the construction of norm-conserving semilocal pseudopotentials for Kohn-Sham models, and prove the existence of optimal pseudopotentials for a family of optimality criteria. Most of our results are proved for the Hartree (also called reduced Hartree-Fock) model, obtained by setting the exchange-correlation energy to zero in the Kohn-Sham energy functional. Extensions to the Kohn-Sham LDA (local density approximation) model are discussed.

1 Introduction

It is a well-known theoretical and experimental fact that the core electrons of an atom are hardly affected by the chemical environment experienced by this atom. Pseudopotential methods are efficient model reduction techniques relying on this observation, which are widely used in electronic structure calculation, especially in solid state physics and materials science, as well as for the simulation of molecular systems containing heavy atoms. In pseudopotential methods, the original all-electron model is replaced by a reduced model explicitly dealing with valence electrons only, while core electrons are frozen in some reference state. The valence electrons are described by valence pseudo-orbitals, and the interaction between the valence electrons and the ionic cores (an ionic core consists of a nucleus and of the associated core electrons) is modeled by a nonlocal operator called a pseudopotential, constructed once and for all from single-atom reference calculations. The reduction of dimensionality obtained by eliminating the core electrons from the explicit calculation results in a much less computationally expensive approach. The pseudopotential has the property that, for isolated atoms, the valence pseudo-orbitals differ from the valence orbitals in the vicinity of the nucleus, *i.e.* in the so-called core region, but coincide with the valence orbitals out of the core region, *i.e.* in the region where the influence of the chemical environment is important. In addition to the reduction of dimensionality mentioned above, an advantage of pseudopotential models is that pseudopotentials are constructed in such a way that the valence pseudo-orbitals oscillate much less than the valence orbitals in the core region, hence can be approximated using smaller planewave bases, or discretized on coarser grids. In addition, pseudopotentials can be used to incorporate relativistic effects in non-relativistic calculations. This is of major interest for the simulation of heavy atoms with relativistic core electrons.

The concept of pseudopotential was first introduced by Hellmann [13] as early as in 1934. Several variants of the pseudopotential method were then developed over the years. Let us mention in particular Kerker's pseudopotentials [16], Troullier-Martins [27] and Kleinman-Bylander [17] norm-conserving pseudopotentials, Vanderbilt ultrasoft pseudopotentials [28], and Goedecker pseudopotentials [9]. Blochl's Projected Augmented Wave (PAW) method [3] can also be interpreted, to some extend, as a pseudopotential method. Although existing pseudopotential methods can be justified by convincing chemical arguments and work satisfactorily in practice, they are obtained by ad hoc procedures, so that the error introduced by the pseudopotential approximation is difficult to quantify *a priori*.

The purpose of this article is to clarify the mathematical framework underlying the construction of semilocal norm-conserving pseudopotentials for Kohn-Sham calculations, and to prove the existence of optimal pseudopotentials for a natural family of optimality criteria. We focus here on theoretical issues; the practical interest of this approach will be investigated in future works. In Section 2, we recall the mathematical structures of all-electron and norm-conserving pseudopotential Kohn-Sham models. In Section 3.2, we provide some results on the spectra of Hartree Hamiltonians for neutral atoms upon which the construction of pseudopotentials is based. Recall that the Hartree model is obtained from the exact Kohn-Sham model by discarding the exchange-correlation energy functional. We then define and analyze in Sections 3.3 to 3.5 the set of admissible semilocal norm-conserving pseudopotentials. After establishing in Section 3.6 some stability results of the Hartree ground state with respect to both external perturbations and small variations of the pseudopotential, we propose in Section 3.7 a new way to construct pseudopotentials, consisting of choosing the best candidate in the set of all admissible pseudopotentials for a given optimality criterion. Most of our results are concerned with the Hartree model. Extensions to the LDA (local density approximation) model are discussed in Section 4. All the proofs are collected in Section 5.

2 Kohn-Sham models

Throughout this article, we use atomic units, in which $\hbar = 1$, $m_e = 1$, $e = 1$ and $4\pi\epsilon_0 = 1$, where $\hbar$ is the reduced Planck constant, m_e the electron mass, e the elementary charge, and ϵ_0 the dielectric permittivity of the vacuum. For simplicity, we only consider here restricted spin-collinear Kohn-Sham models (see [10] for a mathematical analysis of unrestricted and spin-noncollinear Kohn-Sham models) in which the diagonal components $\gamma^{\uparrow\uparrow}$ and $\gamma^{\downarrow\downarrow}$ of the spin-dependent density matrix are equal, and the off-diagonal components $\gamma^{\uparrow\downarrow}$ and $\gamma^{\downarrow\uparrow}$ are both equal to zero. A Kohn-Sham state can therefore be described by a density matrix

$$\gamma = \gamma^{\uparrow\uparrow} + \gamma^{\downarrow\downarrow} = 2\gamma^{\uparrow\uparrow} = 2\gamma^{\downarrow\downarrow}$$

satisfying the following properties:

- $\gamma \in \mathcal{S}(L^2(\mathbb{R}^3))$, where $\mathcal{S}(L^2(\mathbb{R}^3))$ denotes the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$;
- $0 \leq \gamma \leq 2$, which means $0 \leq (\phi, \gamma\phi)_{L^2} \leq 2\|\phi\|_{L^2}^2$ for all $\phi \in L^2(\mathbb{R}^3)$;

- $\mathrm{Tr}\,(\gamma)$ equals the number of electrons in the system.

As we do not consider here molecular models with magnetic fields, we can work in the space $L^2(\mathbb{R}^3)$ of *real-valued* square integrable functions on $\mathbb{R}^3$.

2.1 All electron Kohn-Sham models

Consider a molecular system with N electrons and K point-like nuclei of charges $Z = (z_1, \cdots, z_K) \in \mathbb{N}^K$, located at positions $\mathbf{R} = (\mathbf{R}_1, \cdots, \mathbf{R}_K) \in (\mathbb{R}^3)^K$. The Kohn-Sham ground state of the system is obtained by solving the minimization problem

$$I_{Z,\mathbf{R}} = \inf \left\{ E_{Z,\mathbf{R}}(\gamma),\ \gamma \in \mathcal{K}_N \right\}, \tag{1}$$

where

$$E_{Z,\mathbf{R}}(\gamma) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k |\cdot - \mathbf{R}_k|^{-1} \right) \gamma \right) + \frac{1}{2} D\left(\rho_\gamma, \rho_\gamma\right) + E_{\mathrm{xc}}\left(\rho_\gamma\right), \tag{2}$$

and

$$\mathcal{K}_N := \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \le \gamma \le 2,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty \right\},$$

where $\mathrm{Tr}\,(-\Delta\gamma) := \mathrm{Tr}\,(|\nabla|\gamma|\nabla|)$, with $|\nabla| := (-\Delta)^{1/2}$. Recall that any $\gamma \in \mathcal{K}_N$ has a density $\rho_\gamma \in L^1(\mathbb{R}^3)$, defined by

$$\forall W \in L^\infty(\mathbb{R}^3), \quad \mathrm{Tr}\,(\gamma W) = \int_{\mathbb{R}^3} \rho_\gamma W,$$

which satisfies $\rho_\gamma \ge 0$ in $\mathbb{R}^3$ and $\sqrt{\rho_\gamma} \in H^1(\mathbb{R}^3)$, so that $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. In particular,

$$\mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k |\cdot - \mathbf{R}_k|^{-1} \right) \gamma \right) = \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma) - \sum_{k=1}^{K} z_k \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|}\, d\mathbf{r},$$

where the second term of the right-hand side is well-defined by virtue of Hardy and Hoffmann-Ostenhof inequalities [14]

$$0 \le \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|}\, d\mathbf{r} \le 2N^{1/2} \|\nabla\sqrt{\rho_\gamma}\|_{L^2} \le 2N^{1/2} \mathrm{Tr}\,(-\Delta\gamma)^{1/2} < \infty.$$

The bilinear form $D(\cdot,\cdot)$ in (2) is the Coulomb interaction defined for all $(f, g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$ by

$$D(f, g) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(\mathbf{r})\, g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'. \tag{3}$$

Lastly, the exchange-correlation energy functional E_{xc} depends on the Kohn-Sham model under consideration. We will restrict ourselves to two different Kohn-Sham models, namely the Hartree model, also called the reduced Hartree-Fock model, for which

$$E_{\mathrm{xc}}^{\mathrm{Hartree}}(\rho) = 0,$$

and the Kohn-Sham LDA (local density approximation) model [18], for which

$$E_{\rm xc}^{\rm LDA}(\rho) = \int_{\mathbb{R}^3} \epsilon_{\rm xc}(\rho(\mathbf{r}))\, d\mathbf{r},$$

where for each $\overline{\rho} \in \mathbb{R}_+$, $\epsilon_{\rm xc}(\overline{\rho}) \in \mathbb{R}_-$ is the exchange-correlation energy density of the homogeneous electron gas with uniform density $\overline{\rho}$. The function $\overline{\rho} \mapsto \epsilon_{\rm xc}(\overline{\rho})$ does not have a simple explicit expression, but it has the same mathematical properties as the exchange energy density of the homogeneous electron gas given by $\epsilon_{\rm x}(\overline{\rho}) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \overline{\rho}^{4/3}$.

We are now going to recall some existence and uniqueness results for the Hartree model proved in [4, 24]. Although general results for neutral and positively charged molecular systems are available, we focus here on the case of a single neutral atom, which is of particular interest for the study of pseudopotentials. Weaker results have been obtained for the Kohn-Sham LDA model [1] (see also Section 4).

For convenience, we will call *atom* z the neutral atom with atomic number z.

Proposition 1 (All-electron Hartree model for neutral atoms [4, 24])**.** *Let $z \in \mathbb{N}^*$. The all-electron Hartree model for atom z*

$$I_z^{\rm AA} := \inf \left\{ E_z^{\rm AA}(\gamma),\ \gamma \in \mathcal{K}_z \right\}, \tag{4}$$

where

$$E_z^{\rm AA}(\gamma) = {\rm Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}|}\, d\mathbf{r} + \frac{1}{2} D\left(\rho_\gamma, \rho_\gamma\right),$$

has a minimizer γ_z^0, and all the minimizers of (4) share the same density ρ_z^0. In addition,

1. *the ground state density ρ_z^0 is a radial positive function belonging to $H^2(\mathbb{R}^3) \cap C^{0,1}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0\})$ (hence vanishing at infinity);*
2. *the Hartree Hamiltonian*

$$H_z^{\rm AA} = -\frac{1}{2}\Delta + W_z^{\rm AA}, \quad \textit{where} \quad W_z^{\rm AA} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1},$$

is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and such that $\sigma_{\rm ess}(H_z^{\rm AA}) = [0, +\infty)$;

3. *the minimizers γ_z^0 satisfy the first-order optimality condition*

$$\gamma_z^0 = 2\mathbb{1}_{(-\infty, \epsilon_{z,{\rm F}}^0)}(H_z^{\rm AA}) + \delta,$$

where $\epsilon_{z,{\rm F}}^0 \leq 0$ is the Fermi level (that is the Lagrange multiplier of the constraint ${\rm Tr}\,(\gamma) = z$), and where δ is a finite-rank operator such that $0 \leq \delta \leq 2$ and ${\rm Ran}(\delta) \subset {\rm Ker}(H_z^{\rm AA} - \epsilon_{z,{\rm F}}^0)$;

4. *if $\epsilon_{z,{\rm F}}^0$ is negative and is not an accidentally degenerate eigenvalue of $H_z^{\rm AA}$, then the minimizer γ_z^0 of (4) is unique.*

Remark 2 (on the Fermi level)**.** *Consider, for each $j \in \mathbb{N}^*$, the real number*

$$\varepsilon_{z,j} := \inf_{X_j \in \mathcal{X}_j} \sup_{\phi \in X_j \setminus \{0\}} \frac{\langle \phi | H_z^{\mathrm{AA}} | \phi \rangle}{\|\phi\|_{L^2}^2}, \tag{5}$$

where $\mathcal{X}_j$ is the set of the vector subspaces of $H^1(\mathbb{R}^3)$ of dimension j and $\langle \phi | H_z^{\mathrm{AA}} | \phi \rangle$ the quadratic form associated with the self-adjoint operator H_z^{AA} (whose form domain is $H^1(\mathbb{R}^3)$). According to the minmax principle [21, Theorem XIII.1], $\varepsilon_{z,j}$ is equal to the j^{th} lowest eigenvalue of H_z^{AA} (counting multiplicities) if H_z^{AA} has at least j non-positive eigenvalues (still counting multiplicities), and to $\min(\sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}})) = 0$ otherwise. If z is odd, then $\epsilon^0_{z,\mathrm{F}} = \varepsilon_{z,(z+1)/2}$. If z is even, that is if $z = 2N_{\mathrm{p}}$, where N_{p} is the number of electron pairs, two cases can be distinguished: if $\varepsilon_{z,N_{\mathrm{p}}} = \varepsilon_{z,N_{\mathrm{p}}+1}$, then $\epsilon^0_{z,\mathrm{F}} = \varepsilon_{z,N_{\mathrm{p}}}$, otherwise, any number in the interval $(\varepsilon_{z,N_{\mathrm{p}}}, \varepsilon_{z,N_{\mathrm{p}}+1})$ is an admissible Lagrange multiplier of the constraint $\mathrm{Tr}\,(\gamma) = z$.

Remark 3 (on essential and accidental degeneracies)**.** *Let us clarify the meaning of the last statement of Proposition 1. The mean-field operator H_z^{AA} being invariant with respect to rotations, some of its eigenvalues may be degenerate. More precisely, all its eigenvalues corresponding to p, d, f, ... shells (see Section 3.2) are degenerate, and only those corresponding to s shells are (in general) non-degenerate. Eigenvalue degeneracies due to symmetries are called essential. By contrast, eigenvalues degeneracies of H_z^{AA} which are not due to rotational symmetry are called accidental. For instance, the fact that the 2s and 2p shells of the Hamiltonian $H = -\frac{1}{2}\Delta - \frac{1}{|\cdot|}$ (hydrogen atom) both correspond to the eigenvalue $-1/8$ is an accidental degeneracy. We have checked numerically that $\epsilon^0_{z,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue for any $1 \le z \le 20$. On the other hand, for $z = 21$, $\epsilon^0_{z,\mathrm{F}}$ is very close or equal to zero (see [5]).*

2.2 Kohn-Sham models with norm-conserving pseudopotentials

In pseudopotential calculations, the electrons of each chemical element are partitioned into two categories, core electrons on the one hand and valence electrons on the other hand, according to the procedure detailed in Section 3.4 below. We denote by $N_{z,\mathrm{c}}$ the number of core electrons in atom z, and by $N_{z,\mathrm{v}} = z - N_{z,\mathrm{c}}$ the number of valence electrons. Each chemical element is associated with a bounded nonlocal rotation-invariant self-adjoint operator V_z^{PP}, called the atomic pseudopotential, a core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}} \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, and a core energy $E_{z,\mathrm{c}} \in \mathbb{R}$ which will be precisely defined in Section 3.5. Only valence electrons are explicitly dealt with in pseudopotential calculations. For the molecular system considered in Section 2.1, the pseudopotential approximation of the ground state energy is given by

$$I^{\mathrm{PP}}_{Z,\mathbf{R}} = \inf \left\{ E^{\mathrm{PP}}_{Z,\mathbf{R}}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{\mathrm{v}}} \right\} + \sum_{k=1}^K E_{z_k,\mathrm{c}}, \tag{6}$$

where

$$N_{\mathrm{v}} = N - \sum_{k=1}^K N_{z_k,\mathrm{c}}$$

is the total number of valence electrons in the system ($N_{\rm v} = \sum_{k=1}^K N_{z_k,v}$ if the system is electrically neutral). The Kohn-Sham pseudo-energy functional is

$$E_{Z,\mathbf{R}}^{\rm PP}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + \sum_{k=1}^K \tau_{\mathbf{R}_k} V_{z_k}^{\rm PP} \tau_{-\mathbf{R}_k}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right) + E_{\rm xc}\left(\rho_{\widetilde{\gamma}} + \sum_{k=1}^K \tau_{\mathbf{R}_k}(\widetilde{\rho}_{z_k,{\rm c}}^0)\right),$$

where for all $\mathbf{R} \in \mathbb{R}^3$, $\tau_{\mathbf{R}}$ is the translation operator defined on $L^2(\mathbb{R}^3)$ by $(\tau_{\mathbf{R}}\phi)(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{R})$.

We will describe the precise nature of the atomic pseudopotentials $V_z^{\rm PP}$ in Section 3.5. Let us just mention at this stage that $V_z^{\rm PP}$ is a rotation-invariant operator of the form

$$V_z^{\rm PP} = V_{z,{\rm loc}} + \mathcal{V}_{z,{\rm nl}} \tag{7}$$

where $V_{z,{\rm loc}}$ and $\mathcal{V}_{z,{\rm nl}}$ are respectively the local and nonlocal parts of the pseudopotential operator $V_z^{\rm PP}$. The operator $V_{z,{\rm loc}}$ is a multiplication operator by a real-valued radial function $V_{z,{\rm loc}} \in L^2_{\rm loc}(\mathbb{R}^3)$ satisfying

$$V_{z,{\rm loc}}(\mathbf{r}) \underset{|\mathbf{r}|\to\infty}{\sim} -\frac{N_{z,{\rm v}}}{|\mathbf{r}|}. \tag{8}$$

The operator $\mathcal{V}_{z,{\rm nl}}$ is a $-\Delta$-compact, rotation-invariant, bounded self-adjoint operator on $L^2(\mathbb{R}^3)$ such that

$$\forall \phi \in L^2(\mathbb{R}^3), \quad \left(\text{ess-Supp}(\phi) \subset \mathbb{R}^3 \setminus \overline{B}_{r_{\rm c}}\right) \quad \Rightarrow \quad \left(\mathcal{V}_{z,{\rm nl}}\phi = 0\right), \tag{9}$$

where $r_{\rm c}$ is a positive real number (depending of z) called the core radius of atom z, and where $\overline{B}_{r_{\rm c}}$ is the closed ball of $\mathbb{R}^3$ centered at the origin, with radius $r_{\rm c}$.

The results below are straightforward extensions of the existence and uniqueness results established in [1, 4, 24]. We skip their proofs for brevity.

Proposition 4 (Kohn-Sham models with norm-conserving pseudopotential)**.** *Assume that the molecular system is neutral or positively charged, and that the atomic pseudopotentials satisfy (7)-(9). Then*

1. *the Hartree model (6) with* $E_{\rm xc} = E_{\rm xc}^{\rm Hartree} = 0$ *has a minimizer and all the minimizers share the shame density;*

2. *the Kohn-Sham LDA model (6) with* $E_{\rm xc} = E_{\rm xc}^{\rm LDA}$ *has a minimizer.*

Proposition 5 (Hartree model for neutral atoms and norm-conserving pseudopotentials)**.** *Let* $z \in \mathbb{N}^*$. *If the atomic pseudopotential* $V_z^{\rm PP}$ *satisfies (7)-(9), then the Hartree model*

$$\inf\left\{E_z^{\rm PP}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,{\rm v}}}\right\}, \tag{10}$$

where

$$E_z^{\rm PP}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\rm PP}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right),$$

has a minimizer $\widetilde{\gamma}_z^0$ *and all the minimizers share the same density* $\widetilde{\rho}_z^0$. *In addition,*

1. *the pseudo-density* $\widetilde{\rho}_z^0$ *is a radial positive function belonging to* $H^2(\mathbb{R}^3)$ *(hence vanishing at infinity); ;*

2. *the Hartree pseudo-Hamiltonian*

$$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}, \quad \textit{where} \quad W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1}, \tag{11}$$

corresponding to the pseudopotential V_z^{PP}*, is a bounded below self-adjoint operator on* $L^2(\mathbb{R}^3)$ *with domain* $H^2(\mathbb{R}^3)$ *and such that* $\sigma_{\mathrm{ess}}(H_z^{\mathrm{PP}}) = [0, +\infty)$*;*

3. *the minimizers* $\widetilde{\gamma}_z^0$ *satisfy the first-order optimality condition*

$$\widetilde{\gamma}_z^0 = 2\mathbb{1}_{(-\infty, \widetilde{\epsilon}_{z,\mathrm{F}}^0)}(H_z^{\mathrm{PP}}) + \widetilde{\delta},$$

where $\widetilde{\epsilon}_{z,\mathrm{F}}^0 \leq 0$ *the pseudo Fermi level (the Lagrange multiplier associated with the constraint* $\mathrm{Tr}\,(\widetilde{\gamma}) = N_{z,\mathrm{v}}$*), and where* $\widetilde{\delta}$ *is a finite-rank operator such that* $0 \leq \widetilde{\delta} \leq 2$ *and* $\mathrm{Ran}(\widetilde{\delta}) \subset \mathrm{Ker}(H_z^{\mathrm{PP}} - \widetilde{\epsilon}_{z,\mathrm{F}}^0)$*;*

4. *if* $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ *is negative and is not an accidentally degenerate eigenvalue of* H_z^{PP}*, then the minimizer* $\widetilde{\gamma}_z^0$ *of (4) is unique.*

Remark 6. *We will see in Section 3.5 that, by construction, the Fermi level* $\epsilon_{z,\mathrm{F}}^0$ *and the pseudo Fermi level* $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ *are actually equal, and that if* $\epsilon_{z,\mathrm{F}}^0$ *is negative and is not an accidentally degenerate eigenvalue of* H_z^{AA}*, then* $\widetilde{\epsilon}_{z,\mathrm{F}}^0$ *is (obviously) negative and is not an accidentally degenerate eigenvalue of* H_z^{PP}*.*

3 Analysis of norm-conserving semilocal pseudopotentials

In this section, we restrict ourselves to the Hartree model. Extensions to the Kohn-Sham LDA model are discussed in Section 4.

3.1 Atomic Hamiltonians and rotational invariance

In both all-electron and pseudopotential calculations, atomic Hartree Hamiltonians are self-adjoint operators on $L^2(\mathbb{R}^3)$ invariant with respect to rotations around the nucleus (assumed located at the origin). These operators are therefore block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ associated with the eigenspaces of the operator $\mathbf{L}^2$ (the square of the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (-i\nabla)$). More precisely, the Hilbert space $L^2(\mathbb{R}^3)$ can be decomposed as the direct sum of the pairwise orthogonal subspaces $\mathcal{H}_l := \mathrm{Ker}(\mathbf{L}^2 - l(l+1))$:

$$L^2(\mathbb{R}^3) = \bigoplus_{l \in \mathbb{N}} \mathcal{H}_l. \tag{12}$$

It is convenient to introduce the spaces

$$L_{\mathrm{o}}^2(\mathbb{R}) = \left\{ f \in L^2(\mathbb{R}) \mid f(-r) = -f(r) \text{ a.e.} \right\}$$

(odd square integrable functions on $\mathbb{R}$) and

$$L^2_{\rm r}(\mathbb{R}^3) = \left\{ u \in L^2(\mathbb{R}^3) \mid u \text{ is radial} \right\}$$

(radial square integrable functions on $\mathbb{R}^3$). To any $u \in L^2_{\rm r}(\mathbb{R}^3)$ is associated a (unique) function $R_u \in L^2_{\rm o}(\mathbb{R})$ such that

$$u(\mathbf{r}) = \frac{R_u(|\mathbf{r}|)}{\sqrt{2\pi}|\mathbf{r}|} \quad \text{for a.e. } \mathbf{r} \in \mathbb{R}^3.$$

When there is no ambiguity, we will also denote by

$$u(r) = \frac{R_u(r)}{\sqrt{2\pi} r} \quad \text{for a.e. } r \in \mathbb{R}$$

($r \mapsto u(r)$ then is an even function of r, belonging to the weighted L^2 space $L^2\left(\mathbb{R}, r^2 dr\right)$). It is easily checked that the mapping

$$\mathcal{R} : L^2_{\rm r}(\mathbb{R}^3) \ni u \mapsto R_u \in L^2_{\rm o}(\mathbb{R})$$

is unitary. For $s \in \mathbb{R}$, we denote by

$$H^s_{\rm r}(\mathbb{R}^3) \quad \text{and} \quad H^s_{\rm o}(\mathbb{R})$$

the subspaces of the Sobolev spaces $H^s(\mathbb{R}^3)$ and $H^s(\mathbb{R})$ consisting of radial, and odd distributions respectively, and, for $s \in \mathbb{R}_+$, we denote by $H^s_{\rm loc,r}(\mathbb{R}^3)$ the space of radial locally H^s distributions in $\mathbb{R}^3$.

Lemma 7. *For all $s \in \mathbb{R}_+$ and all $u \in H^s_{\rm r}(\mathbb{R}^3)$, we have that $R_u \in H^s_{\rm o}(\mathbb{R})$. In addition, the mapping $H^s_{\rm r}(\mathbb{R}^3) \ni u \mapsto R_u \in H^s_{\rm o}(\mathbb{R})$ is unitary.*

Denoting by $P_l \in \mathcal{S}(L^2(\mathbb{R}^3))$ the orthogonal projector on $\mathcal{H}_l$, the spaces $\mathcal{H}_l = \text{Ran}(P_l)$ are given by

$$\mathcal{H}_l = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}\, v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m \left(\frac{\mathbf{r}}{|\mathbf{r}|} \right) \,\middle|\, v_{l,m} \in L^2_{\rm o}(\mathbb{R}),\ \forall -l \leq m \leq l \right\},$$

where $(\mathcal{Y}_l^m)_{l \geq 0,\, -l \leq m \leq l}$ are the real spherical harmonics [30], normalized in such a way that

$$\int_{\mathbb{S}^2} \mathcal{Y}_l^m \mathcal{Y}_{l'}^{m'} = \delta_{ll'} \delta_{mm'},$$

where $\mathbb{S}^2$ is the unit sphere of $\mathbb{R}^3$. Clearly,

$$\forall v_l \in \mathcal{H}_l, \quad \|v_l\|^2_{L^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{L^2(\mathbb{R})}.$$

We also have for all $s \in \mathbb{R}_+$,

$$H^s(\mathbb{R}^3) = \bigoplus_{l \in \mathbb{N}} \left(\mathcal{H}_l \cap H^s(\mathbb{R}^3) \right),$$

$$\mathcal{H}_l \cap H^s(\mathbb{R}^3) = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}\, v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right) \;\middle|\; v_{l,m} \in H^s_{\mathrm{o}}(\mathbb{R}),\ \forall -l \le m \le l \right\},$$

$$\forall v_l \in \mathcal{H}_l \cap H^1(\mathbb{R}^3), \quad \|v_l\|^2_{H^1(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{H^1(\mathbb{R})} + l(l+1) \sum_{m=-l}^{l} \|r^{-1} v_{l,m}\|^2_{L^2(\mathbb{R})},$$

$$\forall v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3), \quad \|v_l\|^2_{H^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \left\| -v''_{l,m} + l(l+1) r^{-2} v_{l,m} + v_{l,m} \right\|^2_{L^2(\mathbb{R})}.$$

By rotational invariance, any atomic Hamiltonian H_z is block-diagonal in the decomposition (12), which we write

$$H_z = \bigoplus_{l \in \mathbb{N}} H_{z,l}. \tag{13}$$

3.2 All-electron atomic Hartree Hamiltonians

All-electron atomic Hartree Hamiltonians are Schrödinger operators of the form

$$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}, \tag{14}$$

where W_z^{AA} is the multiplication operator by the radial function

$$W_z^{\mathrm{AA}}(\mathbf{r}) = -\frac{z}{|\mathbf{r}|} + \left(\rho_z^0 \star |\cdot|^{-1}\right)(\mathbf{r}),$$

ρ_z^0 being the radial all-electron atomic Hartree ground state density of atom z (see Proposition 1). The operator $H_{z,l}^{\mathrm{AA}}$ associated with the decomposition (13) is the self-adjoint operator on $\mathcal{H}_l$ with domain $\mathcal{H}_l \cap H^2(\mathbb{R}^3)$ defined for all $v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$ by

$$(H_{z,l}^{\mathrm{AA}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v''_{l,m}(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + W_z^{\mathrm{AA}}(|\mathbf{r}|) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right).$$

This leads us to introduce, for each $l \in \mathbb{N}$, the radial Schrödinger equations

$$-\frac{1}{2}R''(r) + \frac{l(l+1)}{2r^2}R(r) + W_z^{\mathrm{AA}}(r)R(r) = \epsilon R(r), \quad R \in H^1_{\mathrm{o}}(\mathbb{R}), \quad \int_{\mathbb{R}} R^2 = 1. \tag{15}$$

Recall that, for convenience, we also denote by W_z^{AA} the even function from $\mathbb{R}$ to $\mathbb{R}$ such that for all $\mathbf{r} \in \mathbb{R}^3$, $W_z^{\mathrm{AA}}(\mathbf{r}) = W_z^{\mathrm{AA}}(|\mathbf{r}|)$.

The spectral properties of atomic Hartree Hamiltonians which will be useful to construct atomic pseudopotentials are collected in the following proposition.

Proposition 8 (spectrum of atomic Hartree Hamiltonians). *Let $z \in \mathbb{N}^*$ for which $\epsilon_{z,\mathrm{F}}^0 < 0$. The atomic Hartree Hamiltonian H_z^{AA} is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$, and it holds for any $l \in \mathbb{N}$, $\sigma_{\mathrm{ess}}(H_{z,l}^{\mathrm{AA}}) = \sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}}) = [0, +\infty)$. In addition,*

1. *$H_z^{\rm AA}$ has no strictly positive eigenvalues and the set of its non-positive eigenvalues is the union of the non-positive eigenvalues of the operators $H_{z,l}^{\rm AA}$, which are obtained by solving the one-dimensional spectral problem (15);*

2. *for each $l \in \mathbb{N}$, the negative eigenvalues of (15), if any, are simple, and the eigenfunctions associated with the $n^{\rm th}$ eigenvalue have exactly $n-1$ nodes on $(0,+\infty)$;*

3. *for each $l \in \mathbb{N}$, (15) has at most a finite number $n_{z,l}$ of negative eigenvalues. The sequence $(n_{z,l})_{l\in\mathbb{N}}$ is non-increasing and $n_{z,l}=0$ for l large enough. We denote by*

$$l_z^+ = \min\{l \in \mathbb{N} \mid n_{z,l+1} = 0\};$$

4. *denoting by $(\epsilon_{z,n,l})_{1\le n\le n_{z,l}}$ the negative eigenvalues of (15), ranked in increasing order, we have*

$$\forall 0 \le l_1 < l_2 \le l_z^+, \quad \forall n \le n_{z,l_2}, \quad \epsilon_{z,n,l_1} < \epsilon_{z,n,l_2}. \tag{16}$$

We denote by $R_{z,n,l}$ the L^2-normalized eigenfunction associated with the (simple) eigenvalue $\epsilon_{z,n,l}$ of (15) taking positive values for $r > 0$ large enough:

$$R_{z,n,l} \in H^1_{\rm o}(\mathbb{R}), \quad -\frac{1}{2}R''_{z,n,l}(r) + \frac{l(l+1)}{2r^2}R_{z,n,l}(r) + W_z^{\rm AA}(r)R_{z,n,l}(r) = \epsilon_{z,n,l}R_{z,n,l}(r),$$
$$\int_{\mathbb{R}} R_{z,n,l}^2 = 1, \quad R_{z,n,l}(r) > 0 \quad \text{for } r \gg 1.$$

An orthonormal family of eigenfunctions of the negative part of the atomic Kohn-Sham Hamiltonian $H_z^{\rm AA}$ is thus given by

$$\phi_{z,n,l}^m(\mathbf{r}) = \frac{\sqrt{2}\,R_{z,n,l}(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \quad 0 \le l \le l_z^+,\ 1 \le n \le n_{z,l},\ -l \le m \le l.$$

Note that $\phi_{z,n,l}^m \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$.

Remark 9. *The integers l and m are respectively called the azimuthal and magnetic quantum numbers. With the labeling of the eigenvalues of $H_z^{\rm AA}$ we have chosen, the so-called principal quantum number is equal to $(n+l)$. Thus, the 2p and 4d shells of atom z respectively correspond to the eigenvalues $\epsilon_{z,1,1}$ (first eigenvalue of $H_z^{\rm AA}|_{\mathcal{H}_1}$) and $\epsilon_{z,2,2}$ (second eigenvalue of $H_z^{\rm AA}|_{\mathcal{H}_2}$).*

The ground state density matrix γ_z^0 can be written as

$$\gamma_z^0 = \sum_{l=0}^{l_z^+}\sum_{n=1}^{n_{z,l}}\sum_{m=-l}^{l} p_{z,n,l}|\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m|, \tag{17}$$

where $0 \le p_{z,n,l} \le 2$ is the occupation number of the Kohn-Sham orbital $\phi_{z,n,l}^m$. Note that $p_{z,n,l}$ is independent of the magnetic quantum number m. The occupation numbers are such that

$$p_{z,n,l} = 2 \text{ if } \epsilon_{z,n,l} < \epsilon_{z,{\rm F}}^0, \quad 0 \le p_{z,n,l} \le 2 \text{ if } \epsilon_{z,n,l} = \epsilon_{z,{\rm F}}^0, \quad p_{z,n,l} = 0 \text{ if } \epsilon_{z,n,l} > \epsilon_{z,{\rm F}}^0, \tag{18}$$

and

$$\sum_{l=0}^{l_z^+}\sum_{n=1}^{n_{z,l}}(2l+1)p_{z,n,l} = z.$$

We call occupied l-shells of atom z the shells s ($l = 0$), p ($l = 1$), d ($l = 2$), f ($l = 3$), ... for which $n_{z,l} > 0$ and $p_{z,1,l} > 0$. In view of (16)-(18) if a shell l is occupied, then so are all the shells l' with $l' < l$. Denoting by

$$l_z^- = \max\left\{0 \le l \le l_z^+ \mid p_{z,1,l} > 0\right\},$$

we thus obtain that all the shells $l \le l_z^-$ are occupied, and all the shells $l_z^- < l \le l_z^+$ (if any, see Remark 10 below) are unoccupied.

It follows from (17)-(18) that if $\epsilon_{z,\mathrm{F}}^0$ is not an eigenvalue of H_z^{AA} (non-degenerate case in the terminology used in [4]), that is if the highest occupied shell is fully occupied, then the ground state density matrix is unique and is the orthogonal projector

$$\gamma_z^0 = 2\sum_{n,l,m \,\mid\, \epsilon_{z,n,l}<\epsilon_{z,\mathrm{F}}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| \quad \text{(non-degenerate case)}.$$

We also know (see Proposition 1 and Remark 3) that if $\epsilon_{z,\mathrm{F}}^0$ is an eigenvalue ϵ_{z,n_0,l_0} of H_z^{AA} which is negative (degenerate case in the terminology used in [4]), and is not accidentally degenerate, then the ground state density matrix is still unique and is given by

$$\gamma_z^0 = 2\sum_{n,l,m \,\mid\, \epsilon_{z,n,l}<\epsilon_{z,\mathrm{F}}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| + \frac{z-N_{\mathrm{f}}}{2l_0+1}\sum_{m=-l_0}^{l_0} |\phi_{z,n_0,l_0}^m\rangle\langle\phi_{z,n_0,l_0}^m| \quad \text{(degenerate case)},$$

where $N_{\mathrm{f}} = 2\sum_{n,l \,\mid\, \epsilon_{z,n,l}<\epsilon_{z,\mathrm{F}}^0}(2l+1)$ is the number of electrons in the fully occupied shells.

3.3 Atomic semilocal norm-conserving pseudopotentials

Atomic norm-conserving pseudopotentials are operators of the form

$$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l \mathcal{V}_{z,l} P_l, \qquad \text{for some } l_z^- \le l_z \le l_z^+, \tag{19}$$

where $V_{z,\mathrm{loc}} \in H^s_{\mathrm{loc,r}}(\mathbb{R}^3)$ and where we recall that $P_l \in \mathcal{B}(L^2(\mathbb{R}^3))$ is the orthogonal projector on the space $\mathcal{H}_l$. The first term in the right-hand side of (19) therefore is a local operator, while the second term is nonlocal. The structure of the operator $\mathcal{V}_{z,l}$ depends on the nature of the pseudopotential under consideration:

- in semilocal pseudopotentials, $\mathcal{V}_{z,l}$ is a multiplication operator by a function $V_{z,l} \in H^s_{\mathrm{r}}(\mathbb{R}^3)$; otherwise stated, $\mathcal{V}_{z,l}$ is a local operator on $\mathcal{H}_l$;
- in Kleiman-Bylander pseudopotentials, $\mathcal{V}_{z,l}$ is a finite-rank rotation-invariant operator.

We restrict our analysis to semilocal pseudopotentials. The overall regularity of the pseudopotential is governed by the parameter s. For each $0 \leq l \leq l_z$, the function $V_{z,l}$ is supported in a ball of radius $r_{\mathrm{c},l}$. The positive number

$$r_{\mathrm{c}} := \max_{0 \leq l \leq l_z} r_{\mathrm{c},l}$$

is called the core radius.

The operators $H_{z,l}^{\mathrm{PP}}$ involved in the decomposition (13) of the atomic Hartree pseudo-Hamiltonian H_z^{PP} are then given by: for all $0 \leq l \leq l_z$,

$$(H_{z,l}^{\mathrm{PP}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v_{l,m}''(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + (W_{z,\mathrm{loc}} + V_{z,l})(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m \left(\frac{\mathbf{r}}{|\mathbf{r}|} \right),$$

and for all $l > l_z$,

$$(H_{z,l}^{\mathrm{PP}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v_{l,m}''(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + W_{z,\mathrm{loc}}(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m \left(\frac{\mathbf{r}}{|\mathbf{r}|} \right),$$

where

$$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1},$$

$\widetilde{\rho}_z^0$ being the ground state pseudo-density defined in Proposition 5.

The mathematical construction of a semilocal pseudopotential for atom z goes as follows:

Step 1: choose an energy window $\Delta E = (E_-, E_+) \subset \mathbb{R}_-$, which, in particular, defines a partition between core and valence electrons;

Step 2: choose the core radius r_{c} and the Sobolev exponent s, and check that the so-obtained set $\mathcal{M}_{z,\Delta E, r_{\mathrm{c}}, s}$ of admissible pseudopotentials (see Section 3.5) is non-empty;

Step 3: choose the "best" pseudopotential in the set $\mathcal{M}_{z,\Delta E, r_{\mathrm{c}}, s}$.

Steps 1 and 2 are detailed in the next two sections. In Section 3.6, we investigate the stability of the atomic ground state of the pseudopotential model with respect to both external perturbations and variations of the pseudopotential itself. In Section 3.7, we address the existence of optimal pseudopotentials for a variety of optimality criteria.

3.4 Partition between core and valence electrons

As mentioned above, the first task to construct a pseudopotential is to partition the electrons into core and valence electrons. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon_{z,\mathrm{F}}^0 < 0$. This partitioning is made through the choice of an energy window $\Delta E = (E_-, E_+)$, with $-\infty < E_- < E_+ < 0$, containing the Fermi level $\epsilon_{z,\mathrm{F}}^0$ (or *a* Fermi level in the case when the highest occupied energy level is fully occupied, see Remark 2) and such that there exists an integer l_z satisfying $l_z^- \leq l_z \leq l_z^+$ and

$$\forall l \leq l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \overline{\Delta E}\right) = 1, \tag{20}$$

$$\forall l > l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = 0. \tag{21}$$

All the electrons occupying the shells such that $\epsilon_{z,n,l} < E_-$ are considered as core electrons. For each $l \leq l_z$, we denote by $n^\star_{z,l}$, the unique non-negative integer such that $\epsilon_{z,n^\star_{z,l},l} \in \Delta E$. The set $\left\{\epsilon_{z,n^\star_{z,l},l}\right\}_{0\leq l\leq l_z}$ constitute the set of the valence energy levels, which can *a priori* be fully occupied ($E_- < \epsilon_{z,n^\star_{z,l},l} < \epsilon^0_{z,\mathrm{F}}$), partially occupied ($\epsilon_{z,n^\star_{z,l},l} = \epsilon^0_{z,\mathrm{F}}$) or unoccupied ($\epsilon^0_{z,\mathrm{F}} < \epsilon_{z,n^\star_{z,l},l} < E_+$).

Remark 10. *Let us emphasize that it is not clear a priori that one can find energy windows ΔE satisfying (20)-(21). Here again, we need to rely on numerical simulations to establish that our assumptions make sense and are satisfied in practice, at least for some atoms. In another contribution [5] more focused on numerical simulations, we show in particular that for most atoms of the first four rows of the periodic table, $\epsilon^0_{z,\mathrm{F}} < 0$ and energy windows ΔE satisfying (20)-(21) do exist. Besides, for most atoms of the first four rows, atomic Hartree Hamiltonians do not seem to have unoccupied energy levels with negative energies, so that for those atoms, $l_z^+ = l_z^-$ and therefore $l_z = l_z^- = l_z^+$. For instance, it can be checked numerically that the Hartree valence energy levels of the copper atom ($z = 29$) are such that*

$$l_z = 2, \quad n^\star_{z,0} = 4, \quad n^\star_{z,1} = 2, \quad n^\star_{z,2} = 1, \quad E_- < \epsilon_{z,2,1} < \epsilon_{z,4,0} < \epsilon^0_{z,\mathrm{F}} = \epsilon_{z,1,2} < E_+, \quad \text{(for Cu)}.$$

This is the situation depicted on Fig. 1. The core and valence configurations are respectively denoted by $1\mathrm{s}^2\ 2\mathrm{s}^2\ 2\mathrm{p}^6\ 3\mathrm{s}^2$ *and* $3\mathrm{p}^6\ 4\mathrm{s}^2\ 3\mathrm{d}^9$ *in the chemistry literature. Let us observe that the valence configuration of Cu for the Hartree model differs from the one obtained from the N-body Schrödinger equation with infinitesimal Coulomb repulsion [7], that is* $3\mathrm{p}^6\ 3\mathrm{d}^{10}\ 4\mathrm{s}^1$.

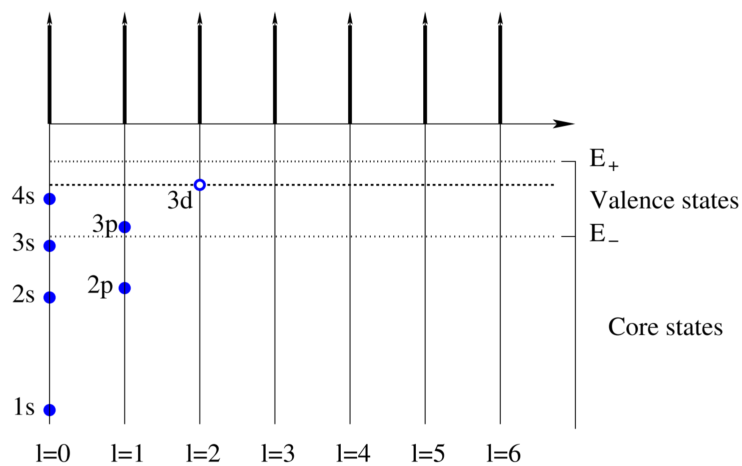

Figure 1: Sketch of the spectra of the operators $H_z^{\mathrm{AA}}|_{\mathcal{H}_l}$ and admissible energy window $\Delta E = (E_-, E_+)$ for the copper atom ($z = 29$). The energy scale is arbitrary. The actual values of the energy levels are the following: $\epsilon_{z,1,0} \simeq -312.78$ Ha (1s), $\epsilon_{z,2,0} \simeq -36.42$ Ha (2s), $\epsilon_{z,1,1} \simeq -31.57$ Ha (2p), $\epsilon_{z,3,0} \simeq -3.716$ Ha (3s), $\epsilon_{z,2,1} \simeq -2.294$ Ha (3p), $\epsilon_{z,4,0} \simeq -5.540 \times 10^{-2}$ Ha (4s), $\epsilon^0_{z,\mathrm{F}} = \epsilon_{z,1,2} \simeq -1.371 \times 10^{-2}$ Ha (3d). The self-consistent Hartree Hamiltonian H_z^{AA} seems to have no negative eigenvalue above the Fermi level $\epsilon^0_{z,\mathrm{F}}$.

We therefore have

$$N_{z,\mathrm{c}} = \sum_{n,l \,|\, \epsilon_{z,n,l} \le E_-} (2l+1) p_{z,n,l} \qquad \text{and} \qquad N_{z,\mathrm{v}} = z - N_{z,\mathrm{c}},$$

where we recall that $N_{z,\mathrm{c}}$ and $N_{z,\mathrm{v}}$ respectively denote the numbers of core and valence electrons. We also introduce the core and valence all-electron Hartree ground state densities, respectively defined as

$$\rho^0_{z,\mathrm{c}}(\mathbf{r}) := 2 \sum_{n,l \,|\, \epsilon_{z,n,l} \le E_-} \sum_{m=-l}^{l} |\phi^m_{z,n,l}(\mathbf{r})|^2 \quad \text{and} \quad \rho^0_{z,\mathrm{v}}(\mathbf{r}) := \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\phi^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2.$$

Note that the core density $\rho^0_{z,\mathrm{c}}$ should not be confused with the core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}}$ mentioned in Section 2.2 and whose expression will be given below (see (32)).

3.5 Admissible pseudopotentials

Let $z \in \mathbb{N}^*$ be such that $\epsilon^0_{z,\mathrm{F}} < 0$, and let $\Delta E = (E_-, E_+)$ be an energy window satisfying the properties (20)-(21). An admissible semilocal norm-conserving pseudopotential with core radius r_c and regularity H^s ($s > 0$) is an operator V^{PP}_z of the form

$$V^{\mathrm{PP}}_z = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l, \qquad \text{for some } l^-_z \le l_z \le l^+_z,$$

for which the radial functions $V_{z,\mathrm{loc}}$ and $V_{z,l}$ satisfy the following properties:

1. **values out of the core region:**

$$\text{in } \mathbb{R}^3 \setminus B_{r_\mathrm{c}}, \quad V_{z,\mathrm{loc}} = -\frac{z}{|\cdot|} + \rho^0_{z,\mathrm{c}} \star |\cdot|^{-1} \quad \text{and} \quad V_{z,l} = 0 \text{ for all } 0 \le l \le l_z; \tag{22}$$

2. **H^s-regularity:**

$$V_{z,\mathrm{loc}} \in H^s_{\mathrm{loc,r}}(\mathbb{R}^3) \quad \text{and for all } 0 \le l \le l_z,\ V_{z,l} \in H^s_\mathrm{r}(\mathbb{R}^3); \tag{23}$$

3. **consistency:** the atomic Hartree pseudo-Hamiltonian

$$H^{\mathrm{PP}}_z = -\frac{1}{2}\Delta + W^{\mathrm{PP}}_z, \qquad \text{where} \qquad W^{\mathrm{PP}}_z = W_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l,$$

   obtained with the pseudopotential V^{PP}_z (see Proposition 5) is such that

$$\mathbb{1}_{(-\infty,E_+)}(H^{\mathrm{PP}}_z) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} |\widetilde{\phi}^m_{z,l}\rangle\langle\widetilde{\phi}^m_{z,l}|, \tag{24}$$

$$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}^0_z \star |\cdot|^{-1}, \qquad \widetilde{\rho}^0_z(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2, \tag{25}$$

where

$$\widetilde{\phi}_{z,l}^m(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_{z,l}(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \tag{26}$$

with, for each $0 \leq l \leq l_z$,

$$\widetilde{R}_{z,l} \in H^1_{\mathrm{o}}(\mathbb{R}), \tag{27}$$

$$-\frac{1}{2}\widetilde{R}''_{z,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (W_{z,\mathrm{loc}}(r) + V_{z,l}(r))\,\widetilde{R}_{z,l}(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_{z,l}(r), \tag{28}$$

$$\int_{\mathbb{R}} \widetilde{R}_{z,l}^2 = 1, \tag{29}$$

$$\widetilde{R}_{z,l} = R_{z,n^\star_{z,l},l} \quad \text{on } (r_{\mathrm{c},l}, +\infty) \text{ for some } 0 < r_{\mathrm{c},l} \leq r_{\mathrm{c}}, \tag{30}$$

$$\widetilde{R}_{z,l} \geq 0 \quad \text{on } (0, +\infty), . \tag{31}$$

We can therefore define the set of admissible semilocal norm-conserving pseudopotentials with energy window $\Delta E = (E_-, E_+)$, core radius r_{c} and regularity H^s, for the atom z as

$$\mathcal{M}_{z,\Delta E, r_{\mathrm{c}}, s} := \left\{ V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l \;\middle|\; \text{such that (22)} - \text{(31) hold} \right\}.$$

Several comments are in order:

- condition (22) implies conditions (8)-(9), so that the existence and uniqueness of the atomic ground state valence pseudo-density $\widetilde{\rho}_z^0$ is guaranteed by Proposition 5 as soon as (22) is satisfied;
- it follows from (27)-(29) and (31) that $\epsilon_{z,n^\star_{z,l},l}$ is the ground state eigenvalue of $H_z^{\mathrm{PP}}|_{\mathcal{H}_l}$ and that the $(2l+1)$ functions $\widetilde{\phi}_{z,l}^m$, $-l \leq m \leq l$, form an orthonormal basis of associated eigenfunctions;
- it also follows from (24) that the $\epsilon_{z,n^\star_{z,l},l}$'s are the only eigenvalues of H_z^{PP} in the energy range $(-\infty, E_+)$. This property is referred to as the *absence of ghost states* in the physics literature;
- out of the core region, (22) is compatible with (28) and (30). Indeed, (28) and (30) imply that

$$\forall \mathbf{r} \in \mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}, \quad \widetilde{\rho}_z^0(\mathbf{r}) = \rho_{z,\mathrm{v}}^0(\mathbf{r}) \quad \text{and} \quad W_{z,\mathrm{loc}}(\mathbf{r}) + V_{z,l}(\mathbf{r}) = W_z^{\mathrm{AA}}(\mathbf{r}),$$

  hence, applying Gauss theorem, that $\widetilde{\rho}_z^0 \star |\cdot|^{-1} = \rho_{z,\mathrm{v}}^0 \star |\cdot|^{-1}$ in $\mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}$, which finally leads to

$$V_{z,\mathrm{loc}} + V_{z,l} = W_z^{\mathrm{AA}} - \rho_{z,\mathrm{v}}^0 \star |\cdot|^{-1} = -\frac{z}{|\cdot|} + \rho_{z,\mathrm{c}}^0 \star |\cdot|^{-1} \quad \text{in } \mathbb{R}^3 \setminus B_{r_{\mathrm{c}}};$$

- the core energies and the core pseudo-densities $\widetilde{\rho}_{0,\mathrm{c}}$ of the atoms appearing in (6) are defined in such a way that for an isolated atom, the pseudopotential calculation gives the same energy as the all-electron model. In the Hartree case, the core energy of atom z is therefore given by

$$\begin{aligned}
E_{z,\mathrm{c}} &= I_z^{\mathrm{AA}} - \inf\left\{E_z^{\mathrm{PP}}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\mathrm{v}}}\right\} \\
&= I_z^{\mathrm{AA}} - \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\mathrm{PP}}\right)\widetilde{\gamma}_z^0\right) - \frac{1}{2}D\left(\widetilde{\rho}_z^0, \widetilde{\rho}_z^0\right) \\
&= I_z^{\mathrm{AA}} - \sum_{l=0}^{l_z}(2l+1)p_{z,n_{z,l}^\star,l}\epsilon_{z,n_{z,l}^\star,l} + \frac{1}{2}D\left(\widetilde{\rho}_z^0, \widetilde{\rho}_z^0\right).
\end{aligned}$$

The core pseudo-density of atom z is defined by

$$\widetilde{\rho}_{z,\mathrm{c}}^0 = \rho_z^0 - \widetilde{\rho}_z^0. \tag{32}$$

Note that atomic core pseudo-densities do not play any role in the Hartree model, since they are only involved in the exchange-correlation energy functional.

The rest of this section is devoted to the study of the set $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon_{z,\mathrm{F}}^0 < 0$ and that $\Delta E = (E_-, E_+)$ is a fixed energy window satisfying (20)-(21). It readily follows from the definition of $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ that

$$\forall 0 < r_\mathrm{c} \leq r_\mathrm{c}' < +\infty, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s} \subset \mathcal{M}_{z,\Delta E,r_\mathrm{c}',s}, \tag{33}$$

$$\forall 0 \leq s \leq s' < +\infty, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s'} \subset \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}. \tag{34}$$

Let

$$r_{z,\Delta E,\mathrm{c}}^- = \max_{0\leq l\leq l_z}\left(\max R_{z,n_{z,l}^\star,l}^{-1}(0)\right) \geq 0$$

be the maximum over $0 \leq l \leq l_z$ of the largest node of the function $R_{z,n_{z,l}^\star,l}$. If $r_\mathrm{c} < r_{z,\Delta E,\mathrm{c}}^-$, then (30) and (31) are obviously inconsistent, and $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s} = \emptyset$. On the other hand, we are going to see that $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is not empty, for any $s \geq 0$, as soon as r_c is large enough. To any potential $W \in L_\mathrm{r}^{3/2}(\mathbb{R}^3)$, we associate the function $\mathcal{T}_W : (0,+\infty) \to \mathbb{R}_-$ defined for all $r > 0$ by

$$\mathcal{T}_W(r) := \inf_{\substack{\phi\,\in\, H_0^1(\Omega(r)) \\ \|\phi\|_{L^2(\Omega(r))}\,=\,1}} \int_{\Omega(r)}\left(\frac{1}{2}|\nabla\phi|^2 + W\phi^2\right),$$

where $\Omega(r) = \mathbb{R}^3 \setminus \overline{B}_r$. We will prove in Section 5.3 that $\mathcal{T}_{W_z^{\mathrm{AA}}}$ is continuous and non-decreasing, and that it maps $(0,+\infty)$ onto $(\varepsilon_{z,1}, 0]$ (where we recall that $\varepsilon_{z,1}$ is the lowest eigenvalue of H_z^{AA}, see (5)).

Lemma 11. *Let $z \in \mathbb{N}^*$ be such that $\epsilon_{z,\mathrm{F}}^0 < 0$. Let $\Delta E = (E_-, E_+)$ be an energy window satisfying (20)-(21). The equation $\mathcal{T}_{W_z^{\mathrm{AA}}}(r) = E_+$ has a unique solution $r_{z,\Delta E,\mathrm{c}}^+ > 0$. In addition, $r_{z,\Delta E,\mathrm{c}}^- < r_{z,\Delta E,\mathrm{c}}^+$ and for all $r_\mathrm{c} \geq r_{z,\Delta E,\mathrm{c}}^+$ and all $s \geq 0$, the set $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is nonempty.*

We were not able to provide a simple characterization of the critical core radius $r^0_{z,\Delta E,\mathrm{c}}$, $r^-_{z,\Delta E,\mathrm{c}} \le r^0_{z,\Delta E,\mathrm{c}} \le r^+_{z,\Delta E,\mathrm{c}}$, such that for all $s \ge 0$,

$$\forall r_\mathrm{c} < r^0_{z,\Delta E,\mathrm{c}}, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s} = \emptyset \quad \text{and} \quad \forall r_\mathrm{c} > r^0_{z,\Delta E,\mathrm{c}}, \quad \mathcal{M}_{z,\Delta E,r_\mathrm{c},s} \neq \emptyset.$$

We can only show, using the same regularization argument as in the proof of Lemma 11, that $r^0_{z,\Delta E,\mathrm{c}}$ is indeed independent of s.

Our next results will be established under the following:

Assumption 1: $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue of H^{AA}_z, $\Delta E = (E_-, E_+)$ satisfies (20)-(21), $r_\mathrm{c} > r^0_{z,\Delta E,\mathrm{c}}$ and $s > 0$.

Consider now the Hilbert space

$$X_{z,\Delta E,r_\mathrm{c},s} = \left\{ v = v_{\mathrm{loc}} + \sum_{l=0}^{l_z} P_l v_l P_l \;\middle|\; (v_{\mathrm{loc}}, (v_l)_{0\le l\le l_z}) \in (H^s_{0,\mathrm{r}}(B_{r_\mathrm{c}}))^{l_z+2} \right\} \equiv (H^s_{0,\mathrm{r}}(B_{r_\mathrm{c}}))^{l_z+2},$$

where $H^s_{0,\mathrm{r}}(B_{r_\mathrm{c}})$ is the closure in $H^s(\mathbb{R}^3)$ of the space of radial, real-valued, C^∞ functions on $\mathbb{R}^3$ with compact supports included in the open ball $B_{r_\mathrm{c}} := \left\{ \mathbf{r} \in \mathbb{R}^3 \,|\, |\mathbf{r}| < r_\mathrm{c} \right\}$, and the affine space

$$\mathcal{X}_{z,\Delta E,r_\mathrm{c},s} = \left\{ V = V_{\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_l P_l \;\middle|\; \text{such that } (22)-(23) \text{ hold} \right\}.$$

Note that

$$\forall V \in \mathcal{X}_{z,\Delta E,r_\mathrm{c},s}, \quad \mathcal{X}_{z,\Delta E,r_\mathrm{c},s} = V + X_{z,\Delta E,r_\mathrm{c},s}.$$

As $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is a subset of $\mathcal{X}_{z,\Delta E,r_\mathrm{c},s}$, we can endow the former set with the topology of the latter, and say that a sequence $(V^{\mathrm{PP}}_{z,k})_{k\in\mathbb{N}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ of admissible pseudopotentials

- strongly converges to some $V \in \mathcal{X}_{z,\Delta E,r_\mathrm{c},s}$ if (with obvious notation)

$$\|V_{z,\mathrm{loc},k} - V_{\mathrm{loc}}\|^2_{H^s} + \sum_{l=0}^{l_z} \|V_{z,l,k} - V_l\|^2_{H^s} \underset{k\to\infty}{\to} 0; \tag{35}$$

- weakly converges to some $V \in \mathcal{X}_{z,\Delta E,r_\mathrm{c},s}$ if

$$\forall V' \in X_{z,\Delta E,r_\mathrm{c},s}, \quad \left(V_{z,\mathrm{loc},k} - V_{\mathrm{loc}}, V'_{\mathrm{loc}}\right)_{H^s} + \sum_{l=0}^{l_z} \left(V_{z,l,k} - V_l, V'_l\right)_{H^s} \underset{k\to\infty}{\to} 0. \tag{36}$$

Theorem 12 (properties of the set of norm-conserving pseudopotentials)**.** *Under Assumption 1, $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ is a nonempty weakly (hence strongly) closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_\mathrm{c},s}$.*

In practice, pseudopotentials are constructed by first selecting optimal (for some criterion) pseudo-orbitals $\widetilde{R}_{z,l}$, $0 \le l \le l_z$, and then deducing from these functions the local and nonlocal components of the atomic pseudopotential using the relations

$$\forall \mathbf{r} \in \mathbb{R}^3 \setminus \{0\}, \quad V_{z,\mathrm{loc}}(\mathbf{r}) + V_{z,l}(\mathbf{r}) = \epsilon_{z,n^\star_{z,l},l} + \frac{1}{2}\frac{\widetilde{R}''_{z,l}(|\mathbf{r}|)}{\widetilde{R}_{z,l}(|\mathbf{r}|)} - \frac{l(l+1)}{2|\mathbf{r}|^2} - \left(\widetilde{\rho}^0_z \star |\cdot|^{-1}\right)(\mathbf{r}),$$

where $\widetilde{\rho}^0_z$ is defined by (26) and (25).

The following lemma is useful to select admissible functions $\widetilde{R}_{z,l}$.

Lemma 13. *Let $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ for some $s > \frac{1}{2}$ (so that the functions $V_{z,\mathrm{loc}}$ and $V_{z,l}$ are continuous). For each $0 \le l \le l_z$, the radial function $\widetilde{R}_{z,l}$, defined by (27)-(31) in is $H^{s+2}_\mathrm{o}(\mathbb{R})$ and*

$$\widetilde{R}_{z,l}(r) = O(r^{l+1}) \quad \text{as} \quad r \to 0.$$

3.6 Some stability results

Let $z, \Delta E, r_\mathrm{c}, s$ satisfying Assumption 1. Let $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ be a reference pseudopotential. It follows from Proposition 5 and the definition of $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ (see also Remark 6) that $\epsilon^0_{z,\mathrm{F}}$ is not an accidentally degenerate eigenvalue of H_z^{PP} and that the ground state pseudo-density matrix $\widetilde{\gamma}^0_z$ corresponding to V_z^{PP} is unique.

We can study the sensitivity of $\widetilde{\gamma}^0_z$ with respect to both an external perturbation and the choice of the pseudopotential by considering the minimization problem

$$\mathcal{E}_{V_z^{\mathrm{PP}}}(v, W) := \inf \left\{ E_{V_z^{\mathrm{PP}}}(\widetilde{\gamma}, v, W),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\mathrm{v}}} \right\}, \tag{37}$$

where the energy functional $E_{V_z^{\mathrm{PP}}}$ is defined on $\mathcal{K}_{N_{z,\mathrm{v}}} \times X_{z,\Delta E,r_\mathrm{c},s} \times \mathcal{C}'$ by

$$E_{V_z^{\mathrm{PP}}}(\widetilde{\gamma}, v, W) := \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\mathrm{PP}} + v\right)\widetilde{\gamma}\right) + \frac{1}{2}D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + \int_{\mathbb{R}^3} \rho_{\widetilde{\gamma}} W,$$

and where we have denoted by

$$\mathcal{C}' = \left\{ W \in L^6(\mathbb{R}^3) \mid \nabla W \in (L^2(\mathbb{R}^3))^3 \right\}$$

the space of potentials with finite Coulomb energies, endowed with the scalar product defined by

$$\forall (W_1, W_2) \in \mathcal{C}' \times \mathcal{C}', \quad (W_1, W_2)_{\mathcal{C}'} = \int_{\mathbb{R}^3} \nabla W_1 \cdot \nabla W_2.$$

For $\eta > 0$ and X a normed vector space, we denote by $B_\eta(X)$ the open ball of X with center 0 and radius η. The following result somehow guarantees the stability of the pseudopotential model with respect to the choice of the pseudopotential.

Proposition 14. *Let $z, \Delta E, r_\mathrm{c}, s$ satisfying Assumption 1. Then, for all $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$, there exists $\eta > 0$ such that for all $(v, W) \in B_\eta(X_{z,\Delta E,r_\mathrm{c},s}) \times B_\eta(\mathcal{C}')$, problem (37) has a unique minimizer $\widetilde{\gamma}_{v,W}(V_z^{\mathrm{PP}})$. Moreover, for each $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$, the function $(v, W) \mapsto \widetilde{\gamma}_{v,W}(V_z^{\mathrm{PP}})$ is real analytic from $B_\eta(X_{z,\Delta E,r_\mathrm{c},s}) \times B_\eta(\mathcal{C}')$ to the space*

$$\mathfrak{S}_{1,1} := \left\{ T \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \cap \mathcal{S}(L^2(\mathbb{R}^3)) \mid |\nabla| T |\nabla| \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \right\},$$

$\mathfrak{S}_1(L^2(\mathbb{R}^3))$ denoting the space of the trace-class operators on $L^2(\mathbb{R}^3)$. For all $v \in X_{z,\Delta E,r_c,s}$, all $W \in \mathcal{C}'$, and all real numbers α and β such that $-\eta\|v\|^{-1}_{X_{z,\Delta E,r_c,s}} < \alpha < \eta\|v\|^{-1}_{X_{z,\Delta E,r_c,s}}$ and $-\eta\|W\|^{-1}_{\mathcal{C}'} < \beta < \eta\|W\|^{-1}_{\mathcal{C}'}$, we have

$$\widetilde{\gamma}_{\alpha v,\beta W}(V_z^{\rm PP}) = \widetilde{\gamma}_z^0 + \sum_{(j,k)\in(\mathbb{N}\times\mathbb{N})\setminus\{(0,0)\}} \alpha^j \beta^k \, \widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP}), \tag{38}$$

where $\widetilde{\gamma}_z^0$ is the ground state density matrix for the pseudopotential $V_z^{\rm PP}$, where the coefficients $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP})$ of the expansion are uniquely defined in $\mathfrak{S}_{1,1}$, and where the series is normally convergent in $\mathfrak{S}_{1,1}$.

In the next section, we will define optimality criteria based on first-order perturbation method for choosing the "best" pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_c,s}$. These criteria will involve the difference between the first-order response of the all-electron model and that of the pseudopotential model to a given external perturbation W. A natural external perturbation is the one obtained by subjecting the atom to an external uniform electric field (Stark effect):

$$W^{\rm Stark}(\mathbf{r}) = -\mathbf{r}\cdot\mathbf{e}, \tag{39}$$

where $\mathbf{e}$ is the unit vector of the vertical axis of the reference frame. As the unperturbed system is rotation-invariant, the direction of the electric field is unimportant. So is its magnitude since we only consider here first-order perturbations (linear responses).

Note that it is not possible to apply the results in Proposition 14 to the perturbation (39) since $W^{\rm Stark}$ is not in $\mathcal{C}'$. In the framework of the linear Schrödinger equation (see e.g. [21] for a detailed analysis of the case of the Hydrogen atom), the spectrum of a molecular Stark Hamiltonian is purely absolutely continuous and equal to $\mathbb{R}$ for all nonzero values of the electric field. The eigenstates of the unperturbed Hamiltonian turn into resonances. On the other hand, the perturbation series is well-defined; its convergence radius is equal to zero, but the energies and widths of the resonances can nonetheless be computed from the perturbation expansion using Borel summation techniques.

For the atomic Hartree model under consideration here, the perturbed energy functional has no minimizer: for all $\beta \neq 0$,

$$\inf\left\{ E_z^{\rm AA}(\gamma) - \beta \int_{\mathbb{R}^3} \rho_\gamma(\mathbf{r}\cdot\mathbf{e}),\ \gamma\in\mathcal{K}_z \right\} = -\infty.$$

The same holds true for the corresponding pseudopotential model for any $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}$. Physically, this corresponds to the fact that the infimum of the energy is obtained by allowing the electrons to go to infinity towards the regions where $W(\mathbf{r}) = -\beta\mathbf{r}\cdot\mathbf{e}$ goes to $-\infty$. As in the linear framework, each term of the perturbation series is well-defined, but the convergence radius of the series is equal to zero. We will only prove here the part of this result we need, namely that the first-order term of the perturbation expansion is well-defined, and, in the pseudopotential case, that the linear response is continuous with respect to the choice of the pseudopotential (see Theorem 15 below). We are not aware of an extension of the theory of resonances to nonlinear mean-field models of Kohn-Sham type.

For $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}$ and $W \in \mathcal{C}'$, we denote by $\widetilde{\gamma}_W^{(k)}(V_z^{\rm PP}) := \widetilde{\gamma}_{0,W}^{(0,k)}(V_z^{\rm PP})$, where the right-hand side is defined in Proposition 14. We also denote by $\gamma_{z,W}^{(k)}$ the $k^{\rm th}$-order perturbation of the all-electron ground state γ_z^0 when atom z is subjected to an external potential $W \in \mathcal{C}'$. A consequence of [4, Theorems 5 and 12] and of the above Proposition 14 is that the linear maps

$$\mathcal{C}' \ni W \mapsto \gamma_{z,W}^{(1)} \in \mathfrak{S}_{1,1} \quad \text{and} \quad \mathcal{C}' \ni W \mapsto \widetilde{\gamma}_W^{(1)}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}, \quad V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}, \tag{40}$$

are continuous.

Theorem 15. *(Stark effect) Let $z, \Delta E, r_c, s$ satisfying Assumption 1. The continuous linear maps defined by (40) can be extended in a unique way to continuous linear maps*

$$\mathcal{Y}_z \ni W \mapsto \gamma_W^{(1)} \in \mathfrak{S}_{1,1} \quad \text{and} \quad \mathcal{Y}_z \ni W \mapsto \widetilde{\gamma}_W^{(1)}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}, \quad V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s}, \tag{41}$$

where $\mathcal{Y}_z$ is the Banach space

$$\mathcal{Y}_z := \mathcal{C}' + L^2_{\rm w} \quad \text{where} \quad L^2_{\rm w} := \left\{ W \in L^2_{\rm loc}(\mathbb{R}^3) \mid \int_{\mathbb{R}^3} |W(\mathbf{r})|^2 e^{-\sqrt{|\epsilon^0_{z,{\rm F}}|}|\mathbf{r}|}\, d\mathbf{r} < \infty \right\}.$$

In addition, $W^{\rm Stark} \in \mathcal{Y}_z$ and the mapping $\mathcal{M}_{z,\Delta E,r_c,s} \ni V_z^{\rm PP} \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}$ is compact.

3.7 Optimization of norm-conserving pseudopotentials

A natural way to choose a pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_c,s}$ is to optimize some criterion $J(V_z^{\rm PP})$ combining the two requirements that the pseudopotential must be as smooth as possible and as transferable as possible. The smoothness requirement leads us to introduce the criterion

$$J_{\rm s}(V_z^{\rm PP}) := \frac{1}{2}\|W_z^{\rm PP}\|^2_{H^s} := \frac{1}{2}\left(\|W_{z,{\rm loc}}\|^2_{H^s} + \sum_{l=0}^{l_z} \|V_{z,l}\|^2_{H^s} \right), \tag{42}$$

where $W_z^{\rm PP}$ is the self-consistent pseudopotential corresponding to the pseudopotential $V_z^{\rm PP}$ (see Proposition 5). Note that it is natural to use the self-consistent pseudopotential $W_z^{\rm PP}$ rather than $V_z^{\rm PP}$ in the right-hand side of (42) since the smoothness of the Kohn-Sham pseudo-orbitals is controlled by $W_z^{\rm PP}$. Let us first state a general result.

Theorem 16. *Let $z, \Delta E, r_c, s$ satisfying Assumption 1. Consider the criterion*

$$J(V_z^{\rm PP}) = \alpha J_{\rm s}(V_z^{\rm PP}) + J_{\rm t}(V_z^{\rm PP}),$$

where the smoothness criterion $J_{\rm s}$ is defined by (42), where the transferability criterion $J_{\rm t} : \mathcal{M}_{z,\Delta E,r_c,s} \to \mathbb{R}$ is a bounded below weakly lower-semicontinuous function, and where $\alpha > 0$ is a parameter allowing one to balance the smoothness and transferability requirements. Then, the optimization problem

$$\inf \left\{ J(V_z^{\rm PP}),\ V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_c,s} \right\} \tag{43}$$

has a minimizer.

Many different transferability criteria $J_{\rm t}$, based on various physical and chemical properties, can be considered. A natural choice is the criterion

$$J_{\rm t}^{\rm Stark}(V_z^{\rm PP}) := \frac{1}{2} \left\| \mathbb{1}_{\mathbb{R}^3\setminus B_{r_{\rm c}}} \left(\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) - \rho^{(1)}_{z,W^{\rm Stark}} \right) \right\|_{\mathcal{C}}^2, \tag{44}$$

where $\rho^{(1)}_{z,W^{\rm Stark}} = \rho_{\gamma^{(1)}_{z,W^{\rm Stark}}}$ and $\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) = \rho_{\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})}$ are respectively the first-order perturbations of the all-electron and pseudo densities of atom z, when the latter is submitted to the Stark potential (39). The Coulomb space $\mathcal{C}$ is defined as

$$\mathcal{C} = \left\{ \rho \in \mathcal{S}'(\mathbb{R}^3) \mid \widehat{\rho} \in L^1_{\rm loc}(\mathbb{R}^3),\ \|\rho\|^2_{\mathcal{C}} := D(\rho,\rho) < \infty \right\},$$

where

$$D(f,g) := 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}(\mathbf{k})}\,\widehat{g}(\mathbf{k})}{|\mathbf{k}|^2}\, d\mathbf{k}. \tag{45}$$

Let us recall that $L^{6/5}(\mathbb{R}^3) \subset \mathcal{C}$, that the definitions (3) and (45) agree for $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$, and that $\mathcal{C}$ is therefore the space of all charge distributions ρ with finite Coulomb energy.

The following lemma shows that the transferability criterion $J_{\rm t}^{\rm Stark}$ is well-defined and falls into the scope of Theorem 16.

Lemma 17. *Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. Then, $J_{\rm t}^{\rm Stark}$ is a well-defined bounded below weakly continuous mapping from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathbb{R}_+$.*

4 Extensions to the Kohn-Sham LDA model

It is probably quite difficult to extend to the LDA model the results established above for the Hartree model. As usual in the mathematical analysis of Kohn-Sham models, the main obstacle is that we do not know whether the atomic ground state density of atom z is unique. We will therefore limit ourselves to comment on the extensions of our main results under some additional assumptions on the Kohn-Sham LDA ground state.

Assuming that the LDA ground state density ρ_z^0 of atom z is unique, hence radial, and that the LDA Fermi level of atom z is negative, it is then easy to show that the properties of the ground state density and of the atomic Hamiltonian listed in Propositions 1 and 8, as well as the result of uniqueness of the ground state density matrix, still hold for the all-electron Kohn-Sham LDA model. Likewise, the results in Proposition 5 are still valid for the LDA model under the assumption that the ground state pseudo-density $\widetilde{\rho}_z^0$ of atom z is unique. Note that the self-consistent potentials are then given, in the all-electron setting, by

$$W_z^{\rm AA} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} + v_{\rm xc}(\rho_z^0),$$

where $v_{\rm xc}(\rho_z^0) = \frac{d\epsilon_{\rm xc}}{d\overline{\rho}}(\rho_z^0)$ is the exchange-correlation potential, and, in the pseudopotential setting, by

$$W_z^{\rm PP} = V_z^{\rm PP} + \widetilde{\rho}_z^0 \star |\cdot|^{-1} + v_{\rm xc}(\widetilde{\rho}_{z,{\rm c}}^0 + \widetilde{\rho}_z^0).$$

Still under the above assumptions, Lemma 11 (nonemptyness of the set $\mathcal{M}_{z,\Delta E,r_c,s}$ of admissible pseudopotentials), Theorem 11 ($\mathcal{M}_{z,\Delta E,r_c,s}$ is a weakly closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_c,s}$), and Theorem 16 (existence of an optimal pseudopotential in an abstract framework) can all be extended to the LDA setting.

Note that, in practice, the calibration of pseudopotentials is made under the assumption that the LDA ground state density (with or without pseudopotential) is radial. The calculations then boil down to solving coupled systems of radial Schrödinger equations (see [5, 17, 27] for details). To the best of our knowledge, no numerical evidence that the radial LDA ground state of an atom might not be unique has been published so far.

The extensions of our results involving nonlinear perturbation theory (Proposition 14, Theorem 15, and Lemma 17) require, on top of the above assumptions, an additional assumption on the uniform coercivity of the Hessian of the energy functional at the unperturbed local minimizer. As the exchange-correlation energy density is not twice differentiable at 0 (it behaves as the function $\mathbb{R}_+ \ni \rho \mapsto -\rho^{4/3} \in \mathbb{R}_-$), it is not clear that such an assumption is satisfied. As already mentioned in [4, Section 5], this technical problem is not encountered in Kohn-Sham calculations with periodic boundary conditions due to the fact that the ground state density then is both bounded and bounded away from zero.

5 Proofs

5.1 Proof of Lemma 7

The three-dimensional Fourier transform of a radial function $u \in L^2_{\rm r}(\mathbb{R}^3)$ is related to the one-dimensional Fourier transform of the function $R_u = \mathcal{R}(u)$ by the simple relation

$$\mathcal{F}_3(u)(\mathbf{k}) = \frac{i}{\sqrt{2\pi}|\mathbf{k}|}\mathcal{F}_1(R_u)(|\mathbf{k}|).$$

The above expression is a special case of the Grafakos-Teschl recursion formula [12]. We therefore have

$$\|u\|^2_{H^s(\mathbb{R}^3)} = \int_{\mathbb{R}^3} (1+|\mathbf{k}|^2)^s |\mathcal{F}_3(u)(\mathbf{k})|^2 \, d\mathbf{k} = \frac{1}{2\pi}\int_{\mathbb{R}^3} \frac{(1+|\mathbf{k}|^2)^s}{|\mathbf{k}|^2} |\mathcal{F}_1(R_u)(|\mathbf{k}|)|^2 \, d\mathbf{k}$$

$$= 2\int_0^\infty (1+k^2)^s |\mathcal{F}_1(R_u)(k)|^2 \, dk = \int_{-\infty}^{+\infty} (1+k^2)^s |\mathcal{F}_1(R_u)(k)|^2 \, dk = \|R_u\|^2_{H^s(\mathbb{R})}.$$

5.2 Proof of Proposition 8

The proof of Proposition 8 is based on the following observation.

Lemma 18. *Let $z \in \mathbb{N}^*$ such that $\epsilon^0_{z,\rm F} < 0$. The Hartree potential $W_z^{\rm AA}$ is a radial increasing negative function of $L^2_{\rm r}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0\})$ converging exponentially fast to* 0.

Proof. The Hartree potential $W_z^{\rm AA}$ satisfies $-\Delta W_z^{\rm AA} = 4\pi(\rho_z^0 - z\delta_0)$, where the ground state density ρ_z^0 is in $\mathcal{C}$ and satisfies $\int_{\mathbb{R}^3} \rho_z^0 = z$. We also know from Proposition 1 that

ρ_z^0 is a radial positive function belonging to $C^\infty(\mathbb{R}^3 \setminus \{0\})$. Therefore, $W_z^{\rm AA}$ is radial and belongs to $C^\infty(\mathbb{R}^3 \setminus \{0\})$, and we infer from Gauss theorem that for all $r > 0$,

$$4\pi r^2 \frac{dW_z^{\rm AA}}{dr}(r) = -4\pi \left(-z + \int_{B_r} \rho_z^0 \right) = 4\pi \int_{\mathbb{R}^3 \setminus B_r} \rho_z^0 > 0,$$

where B_r is the ball of $\mathbb{R}^3$ with center 0 and radius r. Hence, $W_z^{\rm AA}$ is a radial increasing function. Its limit at infinity is necessarily equal to zero since $W_z^{\rm AA} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1}$ with $\rho_z^0 \star |\cdot|^{-1} \in \mathcal{C}' \subset L^6(\mathbb{R}^3)$. As $\epsilon_{z,{\rm F}}^0 < 0$, the ground state density of the atom z is of the form

$$\rho_z^0(\mathbf{r}) = \sum_{i=1}^n p_i |\phi_i(\mathbf{r})|^2,$$

where the occupation numbers p_i are such that $0 \le p_i \le 2$ and $\sum_{i=1}^n p_i = z$, and where the orbitals ϕ_i satisfy

$$\phi_i \in H^2(\mathbb{R}^3), \quad -\frac{1}{2}\Delta\phi_i + W_z^{\rm AA}\phi_i = \epsilon_i \phi_i, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}.$$

As $\epsilon_i \le \epsilon_{z,{\rm F}}^0 < 0$ and $W_z^{\rm AA}$ goes to zero at infinity, we deduce from the maximum principle for second-order elliptic equations (see e.g. [8]) that for each $1 \le i \le n$, $\phi_i \, e^{\sqrt{|\epsilon_{z,{\rm F}}^0|}|\cdot|/2} \in L^\infty(\mathbb{R}^3)$. Therefore, there exists $C_z \in \mathbb{R}_+$ such that

$$\forall \mathbf{r} \in \mathbb{R}^3, \quad 0 < \rho_z^0(\mathbf{r}) \le C_z \, e^{-\sqrt{|\epsilon_{z,{\rm F}}^0|}|\mathbf{r}|}. \tag{46}$$

Hence,

$$\forall r > 0, \quad 0 \le \frac{dW_z^{\rm AA}}{dr}(r) = \frac{1}{r^2} \int_{\mathbb{R}^3 \setminus B_r} \rho_z^0 \le \frac{C_z}{r^2} \int_{\mathbb{R}^3 \setminus B_r} e^{-\sqrt{|\epsilon_{z,{\rm F}}^0|}|\mathbf{r}'|} \, d\mathbf{r}'.$$

Integrating the above inequality leads to

$$\forall r \ge \frac{2}{\sqrt{|\epsilon_{z,{\rm F}}^0|}}, \quad 0 \ge W_z^{\rm AA}(r) \ge -\frac{4\pi r^2 C_z}{\sqrt{|\epsilon_{z,{\rm F}}^0|}} \, e^{-\sqrt{|\epsilon_{z,{\rm F}}^0|} r}.$$

Together with the fact that $W_z^{\rm AA} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} \in L^2_{\rm loc}(\mathbb{R}^3)$, this bound implies that $W_z^{\rm AA} \in L^2_{\rm r}(\mathbb{R}^3)$. $\square$

The proof of Proposition 8 then follows from classical results on the spectra of rotation-invariant Schrödinger operators (see e.g. [21]), which we recall here for completeness. First, as the function $W_z^{\rm AA}$ is in $L^2_{\rm r}(\mathbb{R}^3)$, the operator $W_z^{\rm AA}(1-\Delta)^{-1}|_{\mathcal{H}_l} = (W_z^{\rm AA}(1-\Delta)^{-1})|_{\mathcal{H}_l}$ is Hilbert-Schmidt for each $l \in \mathbb{N}$ by the Kato-Seiler-Simon inequality [22] and the continuity of P_l. Therefore, $W_z^{\rm AA}$ is a compact perturbation of the operator $-\frac{1}{2}\Delta|_{\mathcal{H}_l}$, and we deduce from Weyl's theorem that $\sigma_{\rm ess}(H_{z,l}^{\rm AA}) = \sigma_{\rm ess}(-\frac{1}{2}\Delta|_{\mathcal{H}_l}) = [0, +\infty)$.

The absence of strictly positive eigenvalues of $H_z^{\rm AA}$ is a consequence of Lemma 18 and [21, Theorem XIII.56]. The set of the negative eigenvalues of $H_z^{\rm AA}$ is the union of the sets of the negative eigenvalues of (15) for $l \in \mathbb{N}$; this is a straightforward consequence of the decomposition (13).

The fact that for each $l \in \mathbb{N}$, the negative eigenvalues of (15), if any, are simple and that the eigenfunctions associated with the n^{th} eigenvalue have exactly $n-1$ nodes on $(0, +\infty)$ is a standard result on one-dimensional Schrödinger equations (Sturm's oscillation theory), which can be read in [6, 15] for instance.

Lemma 18, together with [21, Theorem XIII.9], implies that for each $l \in \mathbb{N}$, (15) has at most $(2l+1)^{-1} \int_0^{+\infty} r |W_z^{\text{AA}}(r)| \, dr < \infty$ negative eigenvalues. Since this number is lower than 1 for l large enough, $H_{z,l}^{\text{AA}}$ has no negative eigenvalue for l large enough. The monotonicity of the sequence $(n_{z,l})_{l \in \mathbb{N}}$ readily follows from the minmax principle. So does the last assertion.

5.3 Proof of Lemma 11

Let us first establish a couple of intermediate results.

Lemma 19. *Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. We denote by $\Omega(r) = \mathbb{R}^3 \setminus \overline{B}_r$, by $T_{W,r}$ the self-adjoint operator on $L^2(\Omega(r))$ with domain $H^1_0(\Omega(r)) \cap H^2(\Omega(r))$ defined by $T_{W,r}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^1_0(\Omega(r)) \cap H^2(\Omega(r))$, and by*

$$\mathcal{T}_W(r) := \min\left(\sigma(T_{W,r})\right) = \inf_{\substack{\phi \,\in\, H^1_0(\Omega(r)) \\ \|\phi\|_{L^2(\Omega(r))} \,=\, 1}} \int_{\Omega(r)} \left(\frac{1}{2} |\nabla \phi|^2 + W \phi^2 \right).$$

We also introduce the self-adjoint operator $T_{W,0}$ on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ defined by $T_{W,0}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^2(\mathbb{R}^3)$. Then, two situations may occur:

- *either $\min\left(\sigma(T_{W,0})\right) = 0$, in which case the function $\mathcal{T}_W$ is identically equal to zero on $(0, +\infty)$;*
- *or $\min\left(\sigma(T_{W,0})\right) < 0$, in which case there exists $\widetilde{r}_{\mathrm{c}} \in (0, +\infty)$ such that the function $\mathcal{T}_W$ is differentiable, strictly increasing and bijective from $(0, \widetilde{r}_{\mathrm{c}})$ to $\left(\min\left(\sigma(T_{W,0})\right), 0\right)$, and identically equal to zero on $(\widetilde{r}_{\mathrm{c}}, +\infty)$.*

Proof. Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. Since for any $0 < r < r' < \infty$, we have $\Omega(r') \subset \Omega(r)$, the function $\mathcal{T}_W$ is non-decreasing on $(0, +\infty)$. As $\sigma_{\text{ess}}(T_{W,r}) = [0, +\infty)$, we have for all $0 < r < \infty$,

$$0 \geq \mathcal{T}_W(r) \geq \inf_{\phi \in H^1(\mathbb{R}^3) \,|\, \|\phi\|_{L^2} = 1} \int_{\mathbb{R}^3} \left(\frac{1}{2} |\nabla \phi|^2 + \mathbb{1}_{\Omega(r)} W |\phi|^2 \right),$$

and it follows from [21, Theorem XIII.9] that the right-hand side is equal to zero for r large enough.

It also holds that $\sigma_{\text{ess}}(T_{W,0}) = [0, +\infty)$. If $T_{W,0}$ has no negative eigenvalue, then the function $\mathcal{T}_W$ is identically equal to zero by the minmax principle. Otherwise, denoting by ϵ_1 the lowest negative eigenvalue of $T_{W,0}$, we have

$$\lim_{r \to 0} \mathcal{T}_W(r) = \epsilon_1.$$

This follows from the fact that $C_c^\infty(\mathbb{R}^3 \setminus \{0\})$ is dense in $H^1(\mathbb{R}^3)$.

Lastly, for any $r \in (0,+\infty)$ such that $\mathcal{T}_W(r) < 0$, the operator $T_{W,r}$ has a negative non-degenerate ground state eigenvalue and a radial ground state $\phi_{W,r} \in H_0^1(\Omega(r)) \cap H^2(\Omega(r))$ such that $\|\phi_{W,r}\|_{L^2(\Omega(B_r))} = 1$ and $\phi_{W,r} > 0$ in $\Omega(r)$. By the Hopft's maximum principle for second-order linear elliptic equations [8], $\frac{\partial \phi_{W,r}}{\partial r} > 0$ on $\partial\Omega(r) = \partial B_r$. It is then well-known [23] that $\mathcal{T}_W$ is differentiable at r and that

$$\mathcal{T}_W'(r) = -\int_{\partial\Omega(r)} \frac{\partial \phi_{W,r}}{\partial n} = \int_{\partial B_r} \frac{\partial \phi_{W,r}}{\partial r} > 0.$$

Therefore, if $T_{W,0}$ has a negative eigenvalue, then the function $\mathcal{T}_W$ is continuous, there exists $0 < \widetilde{r}_c < +\infty$ such that $\mathcal{T}_W$ is differentiable and strictly increasing on $(0,\widetilde{r}_c)$, and identically equal to zero on $[\widetilde{r}_c,+\infty)$, and $\mathcal{T}_W$ maps $(0,+\infty)$ onto $(\epsilon_1, 0)$. □

It follows in particular from Lemma 19 that, since $W_z^{\rm AA} \in L_{\rm r}^{3/2}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$ by Lemma 18, and $\min(\sigma(H_z^{\rm AA})) < E_+ < 0$, the equation $\mathcal{T}_{W_z^{\rm AA}}(r) = E_+$ has a unique solution $r_{z,\Delta E,{\rm c}}^+$.

The second intermediate result we need is the following.

Lemma 20. *Let $l \in \mathbb{N}$, $s \in \mathbb{R}_+$, $E_+ < 0$ and $W \in L_{\rm r}^{3/2}(\mathbb{R}^3)$ vanishing at infinity and such that $W \in H^s(\Omega(\varepsilon))$, for any $\varepsilon > 0$. Let $R_l \in H_{\rm o}^2(\mathbb{R})$ and $\epsilon_l < E_+$ be such that*

$$-\frac{1}{2}R_l''(r) + \frac{l(l+1)}{2r^2}R_l(r) + W(r)R_l(r) = \epsilon_l R_l(r), \qquad \int_{\mathbb{R}} R_l^2 = 1.$$

Let $r_{\rm c}^+$ be the unique positive real number such that $\mathcal{T}_W(r_{\rm c}^+) = E_+$. Then, for all $r_{\rm c} > r_{\rm c}^+$, there exists $\widetilde{W} \in H_{\rm r}^s(\mathbb{R}^3)$ such that

$$\widetilde{R}_l \in H_{\rm o}^1(\mathbb{R}), \tag{47}$$

$$-\frac{1}{2}\widetilde{R}_l''(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_l(r) + \widetilde{W}(r)\widetilde{R}_l(r) = \epsilon_l \widetilde{R}_l(r), \tag{48}$$

$$\int_{\mathbb{R}} \widetilde{R}_l^2 = 1, \tag{49}$$

$$\widetilde{R}_l = R_l \quad \text{on } (r_{\rm c},+\infty), \tag{50}$$

$$\widetilde{R}_l \geq 0 \quad \text{on } (0,+\infty), \tag{51}$$

$$\sigma\left(\left(-\frac{1}{2}\Delta + \widetilde{W}\right)\bigg|_{\mathcal{H}_l}\right) \setminus \{\epsilon_l\} \subset [E_+,+\infty). \tag{52}$$

Proof. Using the notation and the results in Lemma 19, we see that ϵ_l is an eigenvalue of $(T_{W,0})|_{\mathcal{H}_l}$, so that $E_+ \in (\min(\sigma(T_{W,0})), 0)$, which implies that there exists a unique positive real number $r_{\rm c}^+$ such that $\mathcal{T}_W(r_{\rm c}^+) = E_+$. Let $r_{\rm c} > r_{\rm c}^+$ and $m_{\rm c} = \int_0^{r_{\rm c}} R_l^2$. We denote by R the unique odd function in $H^1(-r_c, r_c)$ such that

$$-\frac{1}{2}R'' + \frac{l(l+1)}{2r^2}R - \epsilon_l R = 0, \quad R(r_{\rm c}) = 1,$$

and by

$$F(d)=\int_0^{r_c-d}R^2(r)dr.$$

Note that the function $u(\mathbf{r})=\frac{r_{\rm c}R(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m(\frac{\mathbf{r}}{|\mathbf{r}|})$ is the unique solution in $H^1(B_{r_{\rm c}})$ to the boundary value problem $-\frac{1}{2}\Delta u-\epsilon_l u=0$ in $B_{r_{\rm c}}$, $u|_{\partial B_{r_{\rm c}}}=\mathcal{Y}_l^m$, and that $F(d)=r_{\rm c}^{-2}\int_{B_{r_{\rm c}-d}}|u|^2$. For all $0<\alpha\ll 1\ll A<\infty$, we introduce

$$\theta_{\alpha,A}^-=\arcsin(\alpha/A),\quad \theta_{\alpha,A}^+=\pi-\arcsin(R_l(r_{\rm c})/A)-\theta_{\alpha,A}^-,$$

$d_{\alpha,A}$ the unique solution in $(0,r_{\rm c})$ of

$$\alpha^2F(d)+A^2\frac{d}{2}\left(1-\frac{\sin(2(\theta_{\alpha,A}^++\theta_{\alpha,A}^-))-\sin(2\theta_{\alpha,A}^-)}{2\theta_{\alpha,A}^+}\right)=m_{\rm c},$$

$$k_{\alpha,A}=\frac{\theta_{\alpha,A}^+}{d_{\alpha,A}},\quad v_{\alpha,A}=\epsilon_l-\frac{k_{\alpha,A}^2}{2},$$

$$\beta_{\alpha,A}^-=\frac{k_{\alpha,A}A\cos(\theta_{\alpha,A}^-)}{2\alpha}-\frac{R'(r_c-d_{\alpha,A})}{2R(r_c-d_{\alpha,A})},\quad \beta_{\alpha,A}^+=\frac{R_l'(r_c)-k_{\alpha,A}A\cos(\theta_{\alpha,A}^++\theta_{\alpha,A}^-)}{2R_l(r_c)}.$$

When $\alpha\to 0^+$ and $A\to+\infty$, the above quantities behave as follows

$$\theta_{\alpha,A}^-\to 0^+,\quad \theta_{\alpha,A}^+\to\pi^-,\quad d_{\alpha,A}\sim\frac{2m_{\rm c}}{A^2},\quad k_{\alpha,A}\sim\frac{\pi A^2}{2m_{\rm c}},\quad v_{\alpha,A}\sim-\frac{\pi^2A^4}{8m_{\rm c}^2},$$
$$\beta_{\alpha,A}^-\sim\frac{\pi A^3}{4m_{\rm c}\alpha},\quad \beta_{\alpha,A}^+\sim\frac{\pi A^3}{4m_{\rm c}R_l(r_{\rm c})}. \tag{53}$$

Consider the function $R_{\alpha,A}\in H_{\rm o}^1(\mathbb{R})$ defined on $(0,+\infty)$ by

$$R_{\alpha,A}=\alpha\frac{R}{R(r_{\rm c}-d_{\alpha,A})}\mathbb{1}_{(0,r_{\rm c}-d_{\alpha,A})}+A\sin\left(k_{\alpha,A}(r-r_{\rm c})+\theta_{\alpha,A}^-+\theta_{\alpha,A}^+\right)\mathbb{1}_{(r_{\rm c}-d_{\alpha,A},r_{\rm c})}+R_l\mathbb{1}_{(r_{\rm c},+\infty)}.$$

It is easily checked that $\widetilde{R}_l=R_{\alpha,A}$ is solution of (47)-(51) for $\widetilde{W}=W_{\alpha,A}\in H_{\rm r}^{-1}(\mathbb{R}^3)$, with radial representation given by

$$W_{\alpha,A}=\beta_{\alpha,A}^-\delta_{r_{\rm c}-d_{\alpha,A}}+\left(v_{\alpha,A}-\frac{l(l+1)}{2r^2}\right)\mathbb{1}_{(r_{\rm c}-d_{\alpha,A},r_{\rm c})}+\beta_{\alpha,A}^+\delta_{r_{\rm c}}+W\mathbb{1}_{(r_{\rm c},+\infty)}.$$

Denoting by

$$H_{\alpha,A}=-\frac{1}{2}\Delta+W_{\alpha,A},$$

we are going to show that for $\alpha>0$ small enough and $A<+\infty$ large enough

$$\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right)\setminus\{\epsilon_l\}\subset(E_+,+\infty).$$

Let $\mu_{\alpha,A}=\min\left(\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right)\setminus\{\epsilon_l\}\right)$. Assume that $\mu_{\alpha,A}\le E_+$. As $\sigma_{\rm ess}(H_{\alpha,A}|_{\mathcal{H}_l})=\mathbb{R}_+$, $\mu_{\alpha,A}$ is a discrete eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$. We denote by $U_{\alpha,A}$ an associated normalized

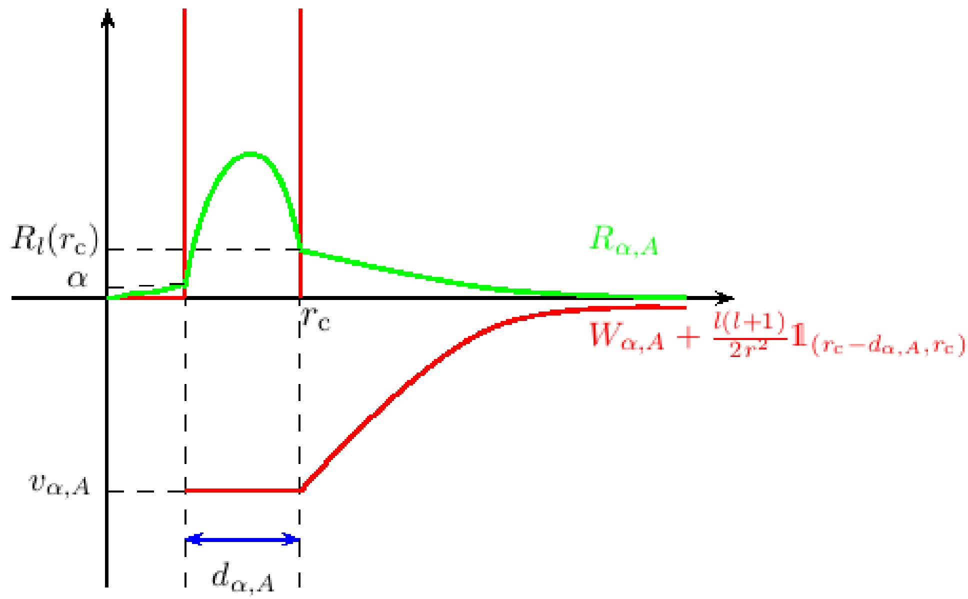

Figure 2: Sketch of the function $R_{\alpha,A}$ (green) and of the potential $W_{\alpha,A}+\frac{l(l+1)}{2r^2}\mathbb{1}_{(r_c-d_{\alpha,A},r_c)}$ (red).

eigenfunction and by $u_{\alpha,A} \in H^1_o(\mathbb{R})$ the odd extension of its radial component multiplied by r. As $\mu_{\alpha,A}$ is in fact the second lowest eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$ (counting multiplicities), the function $u_{\alpha,A}$ satisfies

$$-\frac{1}{2}u''_{\alpha,A} + \frac{l(l+1)}{2r^2}u_{\alpha,A} + W_{\alpha,A}u_{\alpha,A} = \mu_{\alpha,A}u_{\alpha,A},$$

and has exactly one node $r^0_{\alpha,A}$ in $(0,+\infty)$. This node cannot lay in the interval $[r_c,+\infty)$; otherwise, the function $\phi(\mathbf{r}) = U_{\alpha,A}(\mathbf{r})\mathbb{1}_{[r^0_{\alpha,A},+\infty)}(|\mathbf{r}|)\mathcal{Y}^0_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right)$ would belong to $H^1_0(\Omega(r^0_{\alpha,A}))\setminus\{0\}$ and we would have

$$E_+ = \mathcal{T}_W(r_c^+) < \mathcal{T}_W(r^0_{\alpha,A}) \le \frac{\langle\phi|T_{W,r^0_{\alpha,A}}|\phi\rangle}{\langle\phi|\phi\rangle} = \mu_{\alpha,A},$$

which contradicts the assumption that $\mu_{\alpha,A} \le E_+$. It cannot either lay in the interval $(0, r_c - d_{\alpha,A})$; otherwise, as the potential $W_{\alpha,A}$ is equal to zero on this interval, we would have

$$\frac{1}{2}\int_0^{r^0_{\alpha,A}} |u'_{\alpha,A}|^2 + \frac{l(l+1)}{2}\int_0^{r^0_{\alpha,A}} \frac{|u_{\alpha,A}(r)|^2}{r^2}\,dr = \mu_{\alpha,A}\int_0^{r^0_{\alpha,A}} |u_{\alpha,A}|^2 < 0,$$

which is obviously not possible. We therefore have $r_{\alpha,A} \in (r_c - d_{\alpha,A}, r_c)$, and without loss of generality, we can assume that $u_{\alpha,A}$ is positive in the neighborhood of $+\infty$. As $W_{\alpha,A}$ is equal to zero on $(0, r_c - d_{\alpha,A})$, $u_{\alpha,A}$ is negative and concave on this interval, so that $u_{\alpha,A}(r_c - d_{\alpha,A}) < 0$ and $u'_{\alpha,A}((r_c - d_{\alpha,A})^+) < u'_{\alpha,A}((r_c - d_{\alpha,A})^-) < 0$. We therefore have

$$\forall r \in [r_c - d_{\alpha,A}, r_c], \quad u_{\alpha,A} = \widetilde{A}_{\alpha,A}\sin\left(\widetilde{k}_{\alpha,A}(r - (r_c - d_{\alpha,A})) + \widetilde{\theta}_{\alpha,A}\right),$$

with $\widetilde{A}_{\alpha,A} < 0$, $\widetilde{k}_{\alpha,A} = \sqrt{2(\mu_{\alpha,A} - v_{\alpha,A})}$, $0 < \widetilde{\theta}_{\alpha,A} < \pi/2$ and $\pi < \widetilde{k}_{\alpha,A} d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} < 2\pi$. It follows from the jump condition at $r_{\rm c} - d_{\alpha,A}$ and from the fact that $u_{\alpha,A}$ is negative and concave on $(0, r_{\rm c} - d_{\alpha,A})$ that

$$\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{\theta}_{\alpha,A})} = \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} \geq \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+) - u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^-)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} = \beta^-_{\alpha,A}.$$

Thus,

$$\tan(\widetilde{\theta}_{\alpha,A}) \leq \frac{\widetilde{k}_{\alpha,A}}{\beta^-_{\alpha,A}} \leq \frac{2\pi}{\beta^-_{\alpha,A} d_{\alpha,A}} \sim \frac{4\alpha}{A}, \quad \text{when } \alpha \to 0^+ \text{ and } A \to +\infty. \tag{54}$$

We can distinguish two cases:

- case 1: $u'_{\alpha,A}(r_c - 0) < 0$. In this case, $\widetilde{k}_{\alpha,A} d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} > \frac{3\pi}{2}$, which, together with (54), implies that for $\alpha > 0$ small enough and $A > 0$ large enough,

$$\widetilde{k}_{\alpha,A} \geq \frac{5}{4} k_{\alpha,A} \quad \text{or equivalently} \quad \mu_{\alpha,A} \geq \epsilon_l - \frac{9}{16} v_{\alpha,A} \sim \frac{9\pi^2 A^4}{128 m_{\rm c}^2},$$

  which contradicts the assumption that $\mu_{\alpha,A} \leq E_+$;

- case 2: $u'_{\alpha,A}(r_c - 0) \geq 0$. In this case, the function $u_{\alpha,A}$ is positive on $(r_{\rm c}, +\infty)$ and the pair $(u_{\alpha,A}, \mu_{\alpha,A})$ is solution to the spectral problem on $(r_{\rm c}, +\infty)$ with Robin boundary conditions

$$\begin{cases} -\dfrac{1}{2} u''_{\alpha,A}(r) + \dfrac{l(l+1)}{2r^2} u_{\alpha,A}(r) + W u_{\alpha,A}(r) = \mu_{\alpha,A} u_{\alpha,A}(r), \quad r \in (r_{\rm c}, +\infty) \\ u'_{\alpha,A}(r_c + 0) = \left(\dfrac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A} d_{\alpha,A} + \widetilde{\theta}_{\alpha,A})} + \beta^+_{\alpha,A} \right) u_{\alpha,A}(r_c). \end{cases} \tag{55}$$

  When $\alpha \to 0^+$ and $A \to +\infty$, the parameter $\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A} d_{\alpha,A} + \widetilde{\theta}_{\alpha,A})} + \beta^+_{\alpha,A}$ goes to $+\infty$, so that $\mu_{\alpha,A}$ converges to the ground state eigenvalue of $T_{W,r_{\rm c}}|_{\mathcal{H}_l}$, which implies

$$\lim_{\alpha \downarrow 0,\, A \to +\infty} \mu_{\alpha,A} = \mathcal{T}_W(r_c) > \mathcal{T}_W(r_c^+) = E_+.$$

  Choosing $\alpha > 0$ small enough and A large enough, we obtain a contradiction with the assumption that $\mu_{\alpha,A} \leq E_+$.

We therefore have obtained a function $\widetilde{R}_l = R_{\alpha,A} \in H^1_{\rm o}(\mathbb{R})$ and a potential $\widetilde{W} = W_{\alpha,A} \in H^{-1}_{\rm r}(\mathbb{R}^3)$ such that (47)-(52) are satisfied. As $R_{\alpha,A}$ is in $C^\infty(\mathbb{R} \setminus \{\pm(r_{\rm c} - d_{\alpha,A}), \pm r_{\rm c}\})$ and is positive on $(0, +\infty)$, we can construct a sequence $(\widetilde{R}_{l,n})_{n \in \mathbb{N}}$ of odd functions of $C^\infty(\mathbb{R}) \cap H^1_{\rm o}(\mathbb{R})$ positive on $(0, +\infty)$ and converging in $H^1_{\rm o}(\mathbb{R})$ to $R_{\alpha,A}$, such that $\widetilde{R}_{l,n} = R_{\alpha,A} = R_l$ on $(r_{\rm c}, +\infty)$, $\widetilde{R}_{l,n} = R_{\alpha,A}$ on $(0, r_{\rm c} - d_{\alpha,A})$ and $\int_{\mathbb{R}} |\widetilde{R}_{l,n}|^2 = 1$. Consider the sequence of radial potentials defined by

$$\forall n \in \mathbb{N},\ \forall r \in (0, +\infty), \quad \widetilde{W}_n(r) = \epsilon_l + \frac{1}{2} \frac{\widetilde{R}''_{l,n}(r)}{\widetilde{R}_{l,n}(r)} - \frac{l(l+1)}{2r^2}.$$

As $\widetilde{R}_{l,n}(r)$ is bounded away from zero on the interval $[(r_c - d_{\alpha,A})/2, r_c + 1]$ uniformly in n, each $\widetilde{W}_n$ is in $H^s_{\rm r}(\mathbb{R}^3)$ for all $s \geq 0$, and the sequence $(\widetilde{W}_n)_{n\in\mathbb{N}}$ converges to $W_{\alpha,A}$ in $H^{-1}_{\rm r}(\mathbb{R}^3)$. Consequently, the Rayleigh quotients $\mathbf{R}_n(\phi) = \dfrac{\langle\phi| - \frac{1}{2}\Delta + \widetilde{W}_n|\phi\rangle}{\|\phi\|^2}$ converge to $\mathbf{R}(\phi) = \dfrac{\langle\phi| - \frac{1}{2}\Delta + \widetilde{W}|\phi\rangle}{\|\phi\|^2}$ for any $\phi \in \mathcal{H}_l \cap H^1(\mathbb{R}^3)$, which implies, by the minmax principle, that the $k^{\rm th}$ negative eigenvalue of $\left(-\frac{1}{2}\Delta + \widetilde{W}_n\right)\Big|_{\mathcal{H}_l}$ converges to the $k^{\rm th}$ negative eigenvalue of $\left(-\frac{1}{2}\Delta + W_{\alpha,A}\right)\big|_{\mathcal{H}_l}$ when n goes to infinity. Therefore, for n large enough, conditions (47)-(52) are satisfied for $\widetilde{W} = \widetilde{W}_n$. $\square$

We are now in position to prove the non-emptiness of $\mathcal{M}_{z,\Delta E,r_c,s}$ under the assumptions of Lemma 11. Applying Lemma 20 successively for each $0 \leq l \leq l_z$ with $W = W_z^{\rm AA}$, $R_l = R_{z,n^\star_{z,l},l}$, $\epsilon_l = \epsilon_{z,n^\star_{z,l},l}$ and $r_{\rm c} > r^+_{z,{\rm c}}$, we obtain l_z+1 functions $\widetilde{W}_l \in H^s_{\rm r}(\mathbb{R}^3)$ and l_z+1 functions $\widetilde{R}_l$, satisfying for each $0 \leq l \leq l_z$,

$$\widetilde{R}_l \in H^1_{\rm o}(\mathbb{R}), \tag{56}$$

$$-\frac{1}{2}\widetilde{R}_l''(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_l(r) + \widetilde{W}_l\widetilde{R}_l(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_l(r), \tag{57}$$

$$\int_{\mathbb{R}} \widetilde{R}_l^2 = 1, \tag{58}$$

$$\widetilde{R}_l = R_{z,n^\star_{z,l},l} \quad \text{and} \quad \widetilde{W}_l = W_z^{\rm AA} \quad \text{on } (r_{\rm c}, +\infty), \tag{59}$$

$$\widetilde{R}_l \geq 0 \quad \text{on } (0, +\infty). \tag{60}$$

We then introduce the functions

$$\widetilde{\phi}_l^m(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_l(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \qquad -l \leq m \leq l, \tag{61}$$

and the density

$$\widetilde{\rho}^0(\mathbf{r}) = \sum_{l=0}^{l_z}\sum_{m=-l}^{l} p_{z,n^\star_{z,l},l}|\widetilde{\phi}_l^m(\mathbf{r})|^2,$$

and we consider a sequence $(W_{{\rm loc},k})_{k\geq 1}$ of local potentials in the class $H^s_{\rm r}(\mathbb{R}^3)$ such that $W_{{\rm loc},k} \geq W_z^{\rm AA}$ on $\mathbb{R}^3$, $W_{{\rm loc},k} = W_z^{\rm AA}$ in $\Omega(r_{\rm c})$ and $W_{{\rm loc},k} = k$ on $B_{r_{\rm c}-1/k}$. We finally set

$$V_{{\rm loc},k} = W_{{\rm loc},k} - \widetilde{\rho}^0 \star |\cdot|^{-1} \quad \text{and} \quad \forall 0 \leq l \leq l_z, \quad V_{l,k} = \widetilde{W}_l - W_{{\rm loc},k},$$

and

$$V_k = V_{{\rm loc},k} + \sum_{l=0}^{l_z} P_l V_{l,k} P_l.$$

By construction, the self-adjoint operator

$$H_k = -\frac{1}{2}\Delta + V_k + \widetilde{\rho}^0 \star |\cdot|^{-1},$$

on $L^2(\mathbb{R}^3)$ is rotation-invariant, and for all $0 \le l \le l_z$,

$$\mathbb{1}_{(-\infty,E_+)}(H_k|_{\mathcal{H}_l}) = \mathbb{1}_{(-\infty,E_+)}\left(\left(-\frac{1}{2}\Delta + \widetilde{W}_l\right)\bigg|_{\mathcal{H}_l}\right) = \sum_{m=-l}^{l} |\widetilde{\phi}_l^m\rangle\langle\widetilde{\phi}_l^m|.$$

Lastly, for all $l > l_z$,

$$\min \sigma(H_k|_{\mathcal{H}_l}) \ge \min \sigma\left(-\frac{1}{2}\Delta + W_{\mathrm{loc},k}\right) \underset{k\to\infty}{\longrightarrow} \mathcal{T}_{W_z^{\mathrm{AA}}}(r_{\mathrm{c}}) > \mathcal{T}_{W_z^{\mathrm{AA}}}(r_{z,\mathrm{c}}^+) = E_+.$$

Therefore, for k large enough, $V_k \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$.

5.4 Proof of Theorem 12

Let us prove that $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is weakly closed in the affine space $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. For this purpose, we consider a sequence $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ weakly converging to some V_z^{PP} in $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. We denote by $H_{z,k}^{\mathrm{PP}}$ the Hartree pseudo-Hamiltonian obtained with the pseudopotential $V_{z,k}^{\mathrm{PP}}$ and by $\widetilde{\phi}_{z,l,k}^m$ its eigenfunctions of the form (26). We have for all $k \in \mathbb{N}$,

$$\begin{aligned}
&H_{z,k}^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_k, \qquad H_{z,k}^{\mathrm{PP}}\widetilde{\phi}_{z,l,k}^m = \epsilon_{z,n_{z,l}^\star,l}\widetilde{\phi}_{z,l,k}^m, \qquad \|\widetilde{\phi}_{z,l,k}^m\|_{L^2} = 1, \qquad (62)\\
&\widetilde{\rho}_k(\mathbf{r}) = \sum_{l=0}^{l_z}\sum_{m=-l}^{l} p_{z,n_{z,l}^\star,l}|\widetilde{\phi}_{z,l,k}^m(\mathbf{r})|^2, \qquad v_k = \widetilde{\rho}_k \star |\cdot|^{-1},\\
&W_k = V_{z,\mathrm{loc},k} + v_k + \sum_{l=0}^{l_z} P_l V_{z,l,k} P_l.
\end{aligned}$$

Note that for all $0 \le l \le l_z$, $-l \le m \le l$, and $k \in \mathbb{N}$, we have $\widetilde{\phi}_{z,l,k}^m = \phi_{z,n_{z,l}^\star,l}^m$ on $\mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}$ and

$$(W_k\widetilde{\phi}_{z,l,k}^m)(\mathbf{r}) = \left| \begin{array}{ll} W_z^{\mathrm{AA}}(\mathbf{r})\phi_{z,n_{z,l}^\star,l}^m(\mathbf{r}) & \text{if } |\mathbf{r}| \ge r_{\mathrm{c}},\\ (V_{z,\mathrm{loc},k}(\mathbf{r}) + v_k(\mathbf{r}) + V_{z,l,k}(\mathbf{r}))\widetilde{\phi}_{z,l,k}^m(\mathbf{r}) & \text{if } |\mathbf{r}| < r_{\mathrm{c}}. \end{array}\right.$$

As $\epsilon_{z,n_{z,l}^\star,l} < 0$, $v_k \ge 0$ in $\mathbb{R}^3$, and $\|\widetilde{\phi}_{z,l,k}^m\|_{L^2} = 1$ we obtain, using the Sobolev inequality in $\mathbb{R}^3$, the boundedness of the sequence $(\|V_{z,l,k}\|_{L^2})_{k\in\mathbb{N}}$ and Lemma 18, that for all $k \in \mathbb{N}$,

$$\begin{aligned}
\frac{1}{2}\|\nabla\widetilde{\phi}_{z,l,k}^m\|_{L^2}^2 &= -\langle\widetilde{\phi}_{z,l,k}^m|W_k|\widetilde{\phi}_{z,l,k}^m\rangle + \epsilon_{z,n_{z,l}^\star,l}\\
&\le -\int_{B_{r_{\mathrm{c}}}} (V_{z,\mathrm{loc},k} + V_{z,l,k})|\widetilde{\phi}_{z,l,k}^m|^2 - \int_{\mathbb{R}^3\setminus B_{r_{\mathrm{c}}}} W_z^{\mathrm{AA}}|\phi_{z,n_{z,l}^\star,l}^m|^2\\
&\le \left(\|V_{z,\mathrm{loc},k} + V_{z,l,k}\|_{L^2}\|\widetilde{\phi}_{z,l,k}^m\|_{L^2}^{1/2}\|\widetilde{\phi}_{z,l,k}^m\|_{L^6}^{3/2} + \|W_z^{\mathrm{AA}}\|_{L^\infty(\mathbb{R}^3\setminus B_{r_{\mathrm{c}}})}\right)\\
&\le C(1 + \|\nabla\widetilde{\phi}_{z,l,k}^m\|_{L^2}^{3/2}),
\end{aligned}$$

where the constant C is independent of k. This implies that for all $0 \le l \le l_z$ and all $-l \le m \le l$, the sequence $(\widetilde{\phi}_{z,l,k}^m)_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$. We can therefore extract from $(\widetilde{\phi}_{z,l,k}^m)_{k\in\mathbb{N}}$ a subsequence $(\widetilde{\phi}_{z,l,k_n}^m)_{n\in\mathbb{N}}$ which weakly converges in $H^1(\mathbb{R}^3)$ to some function

$\widetilde{\phi}_{z,l}^m \in H^1(\mathbb{R}^3) \cap \mathcal{H}_l$. As for all $k \in \mathbb{N}$, $\widetilde{\phi}_{z,l,k}^m = \phi_{z,n_{z,l}^\star,l}^m$ in $\mathbb{R}^3 \setminus B_{r_c}$, we can assume, without loss of generality, that the convergence of $(\widetilde{\phi}_{z,l,k_n}^m)_{n\in\mathbb{N}}$ to $\widetilde{\phi}_{z,l}^m$ also holds strongly in $L^p(\mathbb{R}^3)$ for all $1 \le p < 6$ and almost everywhere in $\mathbb{R}^3$. In particular,

$$\forall 0 \le l, l' \le l_z, \quad \forall -l \le m \le l, \quad \forall -l' \le m' \le l', \quad \int_{\mathbb{R}^3} \widetilde{\phi}_{z,l}^m \widetilde{\phi}_{z,l'}^{m'} = \delta_{ll'}\delta_{mm'},$$

and the associated functions $\widetilde{R}_{z,l}$ defined by (26) satisfy (27) and (29)-(31). We also infer from the strong convergence of $(\widetilde{\phi}_{z,l,k_n}^m)_{n\in\mathbb{N}}$ to $\widetilde{\phi}_{z,l}^m$ in $L^2(\mathbb{R}^3) \cap L^4(\mathbb{R}^3)$ that the sequence $(\widetilde{\rho}_{k_n})_{n\in\mathbb{N}}$ strongly converges in $L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$, hence in $L^{6/5}(\mathbb{R}^3)$ to the function $\widetilde{\rho}$ defined by

$$\widetilde{\rho}(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n_{z,l}^\star,l} |\widetilde{\phi}_{z,l}^m(\mathbf{r})|^2,$$

which, in turn, implies that the sequence $(v_{k_n})_{n\in\mathbb{N}}$ strongly converges in $\mathcal{C}'$, hence in $L^6(\mathbb{R}^3)$, to the function $v = \widetilde{\rho} \star |\cdot|^{-1}$. Lastly, as $(V_{z,l,k_n})_{n\in\mathbb{N}}$ weakly converges to $V_{z,l}$ in $H^s_{0,r}(B_{r_c})$ for $s > 0$, we can assume without loss of generality that the sequence $(V_{z,l,k_n})_{k_n\in\mathbb{N}}$ strongly converges to $V_{z,l}$ in $L^2(B_{r_c})$. Passing to the limit in (62), we obtain that the functions $\widetilde{R}_{z,l}$ satisfy

$$-\frac{1}{2}\widetilde{R}_{z,l}''(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (v(r) + V_{z,l}(r))\,\widetilde{R}_{z,l}(r) = \epsilon_{z,n_{z,l}^\star,l}\widetilde{R}_{z,l}(r).$$

To conclude that $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_c,s}$, we just need to show that

$$\mathbb{1}_{(-\infty,E_+)}(H_z^{\mathrm{PP}}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} |\widetilde{\phi}_{z,l}^m\rangle\langle\widetilde{\phi}_{z,l}^m|, \tag{63}$$

where $H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + V_z^{\mathrm{PP}} + v$. If this was not the case, there would exists $\lambda < E_+$ and

$$\phi \in H^2(\mathbb{R}^3) \cap \left(\mathrm{Span}\left\{\widetilde{\phi}_{z,l}^m,\ 0 \le l \le l_z,\ -l \le m \le l\right\}\right)^\perp$$

such that $\|\phi\|_{L^2} = 1$ and $H_z^{\mathrm{PP}}\phi = \lambda\phi$. Consider, for n large enough, the function

$$\phi_n = \frac{\phi - \displaystyle\sum_{l=0}^{l_z}\sum_{m=-l}^{l} (\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}\widetilde{\phi}_{z,l,k_n}^m}{\left\|\phi - \displaystyle\sum_{l=0}^{l_z}\sum_{m=-l}^{l} (\widetilde{\phi}_{z,l,k_n}^m, \phi)_{L^2}\widetilde{\phi}_{z,l,k_n}^m\right\|_{L^2}}.$$

We have

$$\phi_n \in H^2(\mathbb{R}^3) \cap \left(\mathrm{Span}\left\{\widetilde{\phi}_{z,l,k_n}^m,\ 0 \le l \le l_z,\ -l \le m \le l\right\}\right)^\perp, \qquad \|\phi_n\|_{L^2} = 1, \tag{64}$$

and

$$\langle\phi_n|H^{\rm PP}_{z,k_n}|\phi_n\rangle = \frac{\lambda + \langle\phi|(V_{z,{\rm loc},k_n}+V_{z,l,k_n}) - (V_{z,{\rm loc}}+V_{z,l})|\phi\rangle + \displaystyle\int_{\mathbb{R}^3}(v_{k_n}-v)\phi^2 - \sum_{l=0}^{l_z}\sum_{m=-l}^{l}\epsilon_{z,n^\star_{z,l},l}|(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}|^2}{\left\|\phi - \displaystyle\sum_{l=0}^{l_z}\sum_{m=-l}^{l}(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}\widetilde{\phi}^m_{z,l,k_n}\right\|^2_{L^2}}.$$

Using the weak convergence of $V^{\rm PP}_{z,k_n}$ to $V^{\rm PP}_z$ in $\mathcal{X}_{z,\Delta E,r_{\rm c},s}$, the strong convergence of v_{k_n} to v in $L^2(\mathbb{R}^3)$ and the strong convergence of $\widetilde{\phi}^m_{z,l,k_n}$ to $\widetilde{\phi}^m_{z,l}$ in $L^2(\mathbb{R}^3)$, we obtain that

$$\lim_{n\to\infty}\langle\phi_n|H^{\rm PP}_{z,k_n}|\phi_n\rangle = \lambda,$$

which, together with (62) and (64), implies that for n large enough, $H^{\rm PP}_{z,k_n}$ has at least $(l_z+1)^2+1$ eigenvalues in $(-\infty,E_+)$, which contradicts the fact that $V^{\rm PP}_{z,k_n}\in\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. Therefore, $V^{\rm PP}_z\in\mathcal{M}_{z,\Delta E,r_{\rm c},s}$, which proves that $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is weakly closed in $\mathcal{X}_{z,\Delta E,r_{\rm c},s}$.

5.5 Proof of Lemma 13

The function $\widetilde{\phi}_{z,l,m}$ is an eigenfunction of the Schrödinger operator $-\frac{1}{2}\Delta + W_{z,{\rm loc}} + V_{z,l}$ on $L^2(\mathbb{R}^3)$, with $W_{z,{\rm loc}}+V_{z,l}\in H^s_{\rm r}(\mathbb{R}^3)$. By elliptic regularity, $\widetilde{\phi}_{z,n,l}\in H^{s+2}(\mathbb{R}^3)$, and therefore $\widetilde{R}_{z,l}\in H^{s+2}_{\rm o}(\mathbb{R})$ in view of Lemma 7. It follows from the unique continuation principle for nonnegative solutions of second-order ordinary differential equations that $\widetilde{R}_{z,l}>0$ on $(0,+\infty)$. The function $\widetilde{R}_{z,l}$ is an odd function which solves a differential equation, with regular singular point, of the form

$$r^2y'' - l(l+1)y + V_l(r)y = 0, \quad \text{with} \quad V_l(0)=0. \tag{65}$$

Its indicial equation is

$$s(s-1) - l(l+1) = 0,$$

with roots $s_1 = l+1$ and $s_2 = -l$. Since $s_1 - s_2 = 2l+1$ is an integer, Fuch's theorem [15, 29] states that the fundamental system of solutions of (65) is

$$\begin{cases} y_1(r) = r^{s_1}p(r) \\ y_2(r) = c\,p(r)r^{s_1}\ln(r) + r^{s_2}q(r), \end{cases}$$

where $p(0)\neq 0$, $q(0)\neq 0$ and c is a constant. As y_2 does not vanish at zero, $\widetilde{R}_{z,l}$ is proportional to y_1.

5.6 Proof of Proposition 14

Observing that

$$E_{V^{\rm PP}_z}(\widetilde{\gamma},v,W) = {\rm Tr}\left(\left(-\frac{1}{2}\Delta + V^{\rm PP}_z\right)\widetilde{\gamma}\right) + \frac{1}{2}D(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}) + {\rm Tr}\,(\widetilde{\gamma}(v+W))$$

allows us to follow the same lines as in the proofs of [4, Theorems 5 and 12] (see also the first point in [4, Section 5]). Indeed, the operator $H^{\rm PP}_z$ has the same spectral properties as the operator H_0 in [4], and the key property on the perturbation that we need to proceed as in [4] is that there exists a constant $C \in \mathbb{R}_+$ such that

$$|\mathrm{Tr}\,(\widetilde{\gamma}(v+W))| \leq C\left(\|v\|_{X_{z,\Delta E,r_c,s}} + \|W\|_{\mathcal{C}'}\right)\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}, \tag{66}$$

for all $(\widetilde{\gamma}, v, W) \in \mathfrak{S}_{1,1} \times X_{z,\Delta E,r_c,s} \times \mathcal{C}'$. Let us prove that (66) actually holds true. On the one hand, we have for all $(\widetilde{\gamma}, W) \in \mathfrak{S}_{1,1} \times \mathcal{C}'$,

$$\begin{aligned}
|\mathrm{Tr}\,(\widetilde{\gamma}W)| &= \left|\mathrm{Tr}\,\left((1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}(1-\Delta)^{-1/2}W\right)\right| \\
&\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\| \\
&\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\|_{\mathfrak{S}_6} \\
&\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|W\|_{L^6} \leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|W\|_{\mathcal{C}'},
\end{aligned}$$

where we have used the Kato-Seiler-Simon inequality [22] for $p = 6$. Likewise, we have for all $(\widetilde{\gamma}, v) \in \mathfrak{S}_{1,1} \times X_{z,\Delta E,r_c,s}$,

$$\begin{aligned}
|\mathrm{Tr}\,(\widetilde{\gamma}v)| &= \left|\mathrm{Tr}\,\left(\left(v_{\mathrm{loc}} + \sum_{l=0}^{l_z} P_l v_l P_l\right)\widetilde{\gamma}\right)\right| \\
&\leq \left|\mathrm{Tr}\,\left((1-\Delta)^{-1/2}v_{\mathrm{loc}}(1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\
&\quad + \sum_{l=0}^{l_z}\left|\mathrm{Tr}\,\left(P_l(1-\Delta)^{-1/2}v_l(1-\Delta)^{-1/2}P_l(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\
&\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\left(\|v_{\mathrm{loc}}\|_{L^2} + \sum_{l=0}^{l_z}\|v_l\|_{L^2}\right) \leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|v\|_{X_{z,\Delta E,r_c,s}},
\end{aligned}$$

where we have used that the P_l's commute with the Laplace operator and the fact that for all $w \in L^2(\mathbb{R}^3)$,

$$\|(1-\Delta)^{-1/2}w(1-\Delta)^{-1/2}\| \leq \||w|^{1/2}(1-\Delta)^{-1/2}\|^2 \leq \||w|^{1/2}(1-\Delta)^{-1/2}\|_{\mathfrak{S}_4}^2 \leq C\|w\|_{L^2},$$

by the Kato-Seiler-Simon inequality for $p = 4$.

Proceeding as in the proofs of Theorems 5 (non-degenerate case) and 12 (degenerate case) in [4], we obtain that there exists $\eta > 0$ such that for all $(v, W) \in B_\eta(X_{z,\Delta E,r_c,s}) \times B_\eta(\mathcal{C}')$, problem (37) has a unique minimizer $\widetilde{\gamma}_{v+W}(V_z^{\mathrm{PP}})$ and that, for each $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_c,s}$, the function $(v+W) \mapsto \widetilde{\gamma}_{v+W}(V_z^{\mathrm{PP}})$ is real analytic from $B_\eta(X_{z,\Delta E,r_c,s}) + B_\eta(\mathcal{C}')$ to $\mathfrak{S}_{1,1}$. Expanding $\alpha \mapsto \widetilde{\gamma}_{\alpha(v+W)}(V_z^{\mathrm{PP}})$ as

$$\widetilde{\gamma}_{\alpha(v+W)}(V_z^{\mathrm{PP}}) = \widetilde{\gamma}_z^0 + \sum_{k=1}^{+\infty}\alpha^k\gamma_{v+W}^{(k)}(V_z^{\mathrm{PP}}),$$

the coefficients $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\mathrm{PP}})$ in (38) are connected to the coefficients $\gamma_{v+W}^{(k)}(V_z^{\mathrm{PP}})$ in the above expansion by the relation

$$\gamma_{\alpha v+\beta W}^{(k)}(V_z^{\mathrm{PP}}) = \sum_{j=0}^{k}\alpha^j\beta^{k-j}\widetilde{\gamma}_{v,W}^{(j,k-j)}(V_z^{\mathrm{PP}}).$$

5.7 Proof of Theorem 15

It suffices to prove the results in the degenerate case, since, in this setting, the non-degenerate case can be seen as a special case of the degenerate case (take $N_{\rm p} = 0$ in [4, Section 4]). We can also restrict ourselves to the pseudopotential case, as the all-electron case works the same.

Let $V_{\rm ref} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ be a reference pseudopotential fixed once and for all and $M \in \mathbb{R}_+$. We are going to establish a series of uniform bounds valid for all $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ satisfying

$$\|V_z^{\rm PP} - V_{\rm ref}\|_{X_{z,\Delta E,r_{\rm c},s}} \le M. \tag{67}$$

In the sequel, we will denote by C_M constants depending on $V_{\rm ref}$ and on M, but not on $V_z^{\rm PP}$. It follows from the arguments used in Section 5.4 that the pseudo-orbitals associated with $V_z^{\rm PP}$ satisfy

$$\max_{0\le l\le l_z} \max_{|m|\le l} \|\widetilde{\phi}_{z,l}^m\|_{H^1} \le C_M,$$

which implies that $\|\widetilde{\rho}_z^0\|_{L^1\cap L^3} \le C_M$, and therefore that $\|\widetilde{\rho}_z^0 \star |\cdot|^{-1}\|_{L^\infty} \le C_M$, from which we infer that

$$\max_{0\le l\le l_z} \|W_{z,{\rm loc}} + V_{z,l}\|_{L^{3/2}} \le C_M, \tag{68}$$

and finally that

$$\max_{0\le l\le l_z} \max_{|m|\le l} \|\widetilde{\phi}_{z,l}^m\|_{L^\infty} \le 2 \max_{0\le l\le l_z} \max_{|m|\le l} \|\widetilde{\phi}_{z,l}^m\|_{H^2} \le C_M. \tag{69}$$

Using the fact that $W_z^{\rm PP} = W_z^{\rm AA}$ in $\Omega(r_{\rm c})$ and the maximum principle for second-order elliptic equations [8], we obtain that

$$\max_{0\le l\le l_z} \max_{|m|\le l} \|\widetilde{\phi}_{z,l}^m e^{\sqrt{|\epsilon_{z,{\rm F}}^0|}|\cdot|/2}\|_{L^\infty} \le C_M. \tag{70}$$

As in [4], we decompose $L^2(\mathbb{R}^3)$ as the orthogonal sum of the fully occupied, partially occupied, and unoccupied spaces

$$L^2(\mathbb{R}^3) := \mathcal{H}_{\rm f} \oplus \mathcal{H}_{\rm p} \oplus \mathcal{H}_{\rm u}, \tag{71}$$

where $\mathcal{H}_{\rm f} = {\rm Ran}(\mathbb{1}_{(-\infty,\epsilon_{z,{\rm F}}^0)}(H_z^{\rm PP}))$, $\mathcal{H}_{\rm p} = {\rm Ran}(\mathbb{1}_{\{\epsilon_{z,{\rm F}}^0\}}(H_z^{\rm PP}))$ and $\mathcal{H}_{\rm u} = {\rm Ran}(\mathbb{1}_{(\epsilon_{z,{\rm F}}^0,+\infty)}(H_z^{\rm PP}))$, and where $P_{\rm f}$, $P_{\rm p}$ and $P_{\rm u}$ are the orthogonal projectors from $L^2(\mathbb{R}^3)$ to $\mathcal{H}_{\rm f}$, $\mathcal{H}_{\rm p}$ and $\mathcal{H}_{\rm u}$ respectively. We then introduce

- the spaces

$$\mathcal{A}_{\rm ux} := \left\{ A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \mid (P_{\rm u}(H_z^{\rm PP} - \epsilon_{\rm F}^0)P_{\rm u})^{1/2} A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \right\},$$

  for ${\rm x} \in \{{\rm f}, {\rm p}\}$, endowed with the inner product

$$(A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} := {\rm Tr}\,(A_{\rm ux}^* P_{\rm u}(H_z^{\rm PP} - \epsilon_{\rm F}^0)P_{\rm u} B_{\rm ux});$$

- the finite dimensional spaces

$$\mathcal{A}_{\rm pf} := \mathcal{B}(\mathcal{H}_{\rm f}, \mathcal{H}_{\rm p}) \quad \text{and} \quad \mathcal{A}_{\rm pp} := \{A_{\rm pp} \in \mathcal{S}(\mathcal{H}_{\rm p}) \mid {\rm Tr}\,(A_{\rm pp}) = 0\};$$

- the product space
$$\mathcal{A} := \mathcal{A}_{\rm uf} \times \mathcal{A}_{\rm up} \times \mathcal{A}_{\rm pf} \times \mathcal{A}_{\rm pp},$$
which we endow with the inner product
$$(A,B)_{\mathcal{A}} = \sum_{\rm x \in \{f,p\}} (A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} + \sum_{\rm x\in\{f,p\}} {\rm Tr}\,\left(A_{\rm px} B_{\rm px}^*\right).$$

Note that the decomposition (71), as well as the space $\mathcal{A}$, depend on $V_z^{\rm PP}$. Following [4, Eq. (43)], let us first show that the continuous linear map

$$\begin{aligned} \zeta :\ & \mathcal{C}' \to \mathcal{A}' \\ & W \mapsto -(P_{\rm u} W P_{\rm f}, P_{\rm u} W P_{\rm p} \Lambda, (2-\Lambda) P_{\rm p} W P_{\rm f}, P_{\rm p} W P_{\rm p}), \end{aligned}$$

where Λ is the diagonal matrix containing the partial occupation numbers at the Fermi level, can be extended in a unique way to a continuous linear map from $\mathcal{C}' + L^2_{\rm w}$ to $\mathcal{A}'$. We first observe that for all $W \in C^\infty_{\rm c}(\mathbb{R}^3)$ (where $C^\infty_{\rm c}(\mathbb{R}^3)$ is the space of the C^∞ functions on $\mathbb{R}^3$ with compact support), and all $A \in \mathcal{A}$,

$$\begin{aligned} |{\rm Tr}\,((P_{\rm u} W P_{\rm f})^* A_{uf})| &= |{\rm Tr}\,(P_{\rm f} W P_{\rm u} A_{\rm uf})| \\ &= \left| {\rm Tr}\,\left(P_{\rm f} W (H_z^{\rm PP} - \epsilon^0_{\rm F})|_{\mathcal{H}_{\rm u}}^{-1/2} (P_{\rm u} (H_z^{\rm PP} - \epsilon^0_{\rm F}) P_{\rm u})^{1/2} A_{\rm uf} \right) \right|, \end{aligned}$$

where $(H_z^{\rm PP} - \epsilon^0_{\rm F})|_{\mathcal{H}_{\rm u}}^{-1/2}$ denotes the bounded operator on $L^2(\mathbb{R}^3)$ block-diagonal in the decomposition (71) identically equal to zero on $\mathcal{H}_{\rm f} \oplus \mathcal{H}_{\rm p}$ and equal to the inverse square root of the invertible positive operator $(H_z^{\rm PP} - \epsilon^0_{\rm F})|_{\mathcal{H}_{\rm u}}$ on $\mathcal{H}_{\rm u}$. As the space $\mathcal{A}_{\rm uf}$ consists of finite-rank operators with rank lower or equal to $N_{\rm f}$, the operator and trace norms are equivalent on this space, and we therefore obtain

$$\begin{aligned} \forall A \in \mathcal{A}, \quad |{\rm Tr}\,((P_{\rm u} W P_{\rm f})^* A_{uf})| &\le (E_+ - \epsilon^0_{z,{\rm F}})^{-1/2} \|P_f W\| \, \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}} \\ &\le (E_+ - \epsilon^0_{z,{\rm F}})^{-1/2} \max_{1 \le n \le N_{\rm f}} \|W \phi_n\|_{L^2} \, \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}, \end{aligned}$$

where $(\phi_n)_{1\le n \le N_{\rm f}}$ is an orthonormal basis of $\mathcal{H}_{\rm f}$. Similar arguments applied to the other components of $\zeta(W)$ lead to

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \le C_M \max_{0 \le l \le l_z,\, -l \le m \le l} \|W \widetilde{\phi}^m_{z,l}\|_{L^2}.$$

Using (70), we deduce from the above inequality that

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \le C_M \|W\|_{L^2_{\rm w}}.$$

As ζ is continuous from $\mathcal{C}'$ to $\mathcal{A}'$ (see [4]), we also have

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \le C_M \|W\|_{\mathcal{C}' + L^2_{\rm w}}. \tag{72}$$

The space $C^\infty_{\rm c}(\mathbb{R}^3)$ being dense in $\mathcal{C}' + L^2_{\rm w}$, we obtain that the linear map ζ can be extended in a unique way to a continuous linear map from $\mathcal{C}' + L^2_{\rm w}$ to $\mathcal{A}'$.

Let us now consider a sequence $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which weakly converges to some $V_z^{\rm PP}$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. As $V_{z,{\rm loc},k}$ coincides with $-\frac{z}{|\cdot|}+\rho_{z,{\rm c}}^0\star|\cdot|^{-1}$ outside $B_{r_{\rm c}}$, we obtain that $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ converges to $V_z^{\rm PP}$ strongly in $\mathcal{M}_{z,\Delta E,r_{\rm c},s/2}$. To prove the compactness of the mapping $\mathcal{M}_{z,\Delta E,r_{\rm c},s}\ni V_z^{\rm PP}\mapsto\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})\in\mathfrak{S}_{1,1}$, it is therefore sufficient to show that the mapping $V_z^{\rm PP}\mapsto\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP})$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$ for any $s>0$. Let us therefore consider a sequence $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which strongly converges to some $V_z^{\rm PP}$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ and $M\in\mathbb{R}_+$ such that

$$\sup_{k\in\mathbb{N}}\|V_{z,k}^{\rm PP}-V_{\rm ref}\|_{X_{z,\Delta E,r_{\rm c},s}}\le M.$$

Using [4, Eqs. (42)-(43)], (72), the bound

$$\|H_{z,k}^{\rm PP}(1-\Delta)^{-1}\|\le C_M,$$

and the fact that there exists $0<c_M\le C_M<+\infty$ such that

$$\forall(A,A')\in\mathcal{A}\times\mathcal{A},\quad\langle\Theta(A),A\rangle\ge c_M\|A\|_{\mathcal{A}}^2\quad\text{and}\quad\langle\Theta(A),A'\rangle\le C_M\|A\|_{\mathcal{A}}\|A'\|_{\mathcal{A}},$$

where the bilinear form Θ is defined in [4, Eq. (59)], we obtain that

$$\sup_{k\in\mathbb{N}}\|\widetilde{\gamma}^{(1)}_W(V_{z,k}^{\rm PP})\|_{\mathfrak{S}_{1,1}}\le C_M\|W\|_{\mathcal{C}'+L^2_{\rm w}}.\tag{73}$$

Let $\varepsilon>0$ and $W\in C_{\rm c}^\infty(\mathbb{R}^3)$ be such that $\|W-W^{\rm Stark}\|_{\mathcal{C}'+L^2_{\rm w}}\le\varepsilon/(3C_M)$, where C_M is the constant in (73). By the triangular inequality,

$$\begin{aligned}\|\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_{z,k}^{\rm PP})-\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})\|_{\mathfrak{S}_{1,1}}&\le\frac{2\varepsilon}{3}+\|\widetilde{\gamma}^{(1)}_W(V_{z,k}^{\rm PP})-\widetilde{\gamma}^{(1)}_W(V_z^{\rm PP})\|_{\mathfrak{S}_{1,1}}\\&\le\frac{2\varepsilon}{3}+\left\|\lim_{\beta\to0}\beta^{-1}\left(\widetilde{\gamma}_{V_{z,k}^{\rm PP}-V_z^{\rm PP},\beta W}(V_z^{\rm PP})-\widetilde{\gamma}_{0,\beta W}(V_z^{\rm PP})\right)\right\|_{\mathfrak{S}_{1,1}}.\end{aligned}$$

We then infer from the analyticity properties of the mapping $(v,W)\mapsto\widetilde{\gamma}_{v,W}(V^{\rm PP})$ (cf. Proposition 14) that for k large enough, the second term of the right-hand side is lower than $\varepsilon/3$. Therefore, the mapping $V_z^{\rm PP}\mapsto\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$.

5.8 Proof of Theorem 16

Let $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ be a minimizing sequence for (43). As $\alpha>0$ and $J_{\rm t}$ is bounded below, the sequence $(W_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ is bounded for the norm $\|\cdot\|_{H^s}$ defined in (42). As $W_{z,k}^{\rm PP}$ coincides with $W_z^{\rm AA}$ outside $B_{r_{\rm c}}$, we can assume, without loss of generality, that $(W_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ converges to some $W_z^{\rm PP}=W_{z,{\rm loc}}^{\rm PP}+\sum_{l=0}^{l_z}P_lV_{z,l}P_l$, weakly for the norm $\|\cdot\|_{H^s}$, and strongly for the norm $\|\cdot\|_{H^{s-\eta}}$ for any $\eta>0$. We then have

$$\frac{1}{2}\|W_z^{\rm PP}\|_{H^s}^2\le\liminf_{k\to\infty}J_{\rm s}(V_{z,k}^{\rm PP}).\tag{74}$$

Reasoning as in the proof of Theorem 12, we obtain that the ground state density $\widetilde{\rho}_k$ of

$$\inf \left\{ \mathrm{Tr} \left(\left(-\frac{1}{2}\Delta + V_{z,k}^{\mathrm{PP}} \right) \widetilde{\gamma} \right) + \frac{1}{2} D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\mathrm{v}}} \right\}$$

converges, when k goes to infinity, to some $\widetilde{\rho}$ in $H^s(\mathbb{R}^3)$, which is in fact the ground state density associated with the self-consistent pseudopotential W_z^{PP}. This implies that $V_{z,\mathrm{loc},k}^{\mathrm{PP}} = W_{z,\mathrm{loc},k}^{\mathrm{PP}} - \widetilde{\rho}_k \star |\cdot|^{-1}$ weakly converges to $V_{z,\mathrm{loc}}^{\mathrm{PP}} := W_{z,\mathrm{loc}}^{\mathrm{PP}} - \widetilde{\rho} \star |\cdot|^{-1}$ in $H_{\mathrm{loc}}^s(\mathbb{R}^3)$. Therefore, $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ weakly converges in $X_{z,\Delta E,r_\mathrm{c},s}$ to $V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}}^{\mathrm{PP}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$, which belongs to $\mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ by virtue of Theorem 12, and W_z^{PP} is the self-consistent pseudopotential associated with V_z^{PP}. Using (74) and the weak lower-semicontinuity property of J_t, we finally obtain that

$$J(V_z^{\mathrm{PP}}) \leq \liminf_{k\to\infty} J(V_{z,k}^{\mathrm{PP}}),$$

which implies that V_z^{PP} is a minimizer to (43).

5.9 Proof of Lemma 17

Let $(V_{z,k}^{\mathrm{PP}})_{k\in\mathbb{N}}$ be a sequence of elements of $\mathcal{M}_{z,\Delta E,\mathrm{c},s}$ weakly converging to V_z^{PP} in $\mathcal{X}_{z,\Delta E,\mathrm{c},s}$. By Theorem 12, $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$ and by Theorem 15, the sequence $(\widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ strongly converges to $\widetilde{\gamma}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ in $\mathfrak{S}_{1,1}$. Consequently, $(\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $\widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ strongly in $L^{6/5}(\mathbb{R}^3)$, which implies that $(\mathbb{1}_{\mathbb{R}^3\setminus B_{r_\mathrm{c}}} \widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $\mathbb{1}_{\mathbb{R}^3\setminus B_{r_\mathrm{c}}} \widetilde{\rho}^{(1)}_{W^{\mathrm{Stark}}}(V_z^{\mathrm{PP}})$ in $L^{6/5}(\mathbb{R}^3)$, hence in $\mathcal{C}$, which implies that the sequence of non-negative real-numbers $(J_\mathrm{t}^{\mathrm{Stark}}(V_{z,k}^{\mathrm{PP}}))_{k\in\mathbb{N}}$ converges to $J_\mathrm{t}^{\mathrm{Stark}}(V_z^{\mathrm{PP}})$.

References

[1] A. Anantharaman and E. Cancès, *Existence of minimizers for Kohn-Sham models in quantum chemistry*, Ann. Inst. Henri Poincaré 26 (2009) 2425–2455.

[2] S. Benzoni-Gavage and D. Serre, *Multidimensional hyperbolic partial differential equations. First-order systems and applications*, Oxford Univ. Press, Oxford, 2007.

[3] P.E. Blöchl, *Projector augmented-wave method*, Phys. Rev. B 50 (1994) 17953–17978.

[4] E. Cancès and N. Mourad, *A mathematical perspective on density functional perturbation theory*, Nonlinearity 27 (2014) 1999–2033.

[5] E. Cancès and N. Mourad, *A numerical study of the extended Kohn-Sham models for atoms*, in preparation.

[6] R. Courant and D. Hilbert, *Methods of mathematical physics. Vol. I*, Interscience Publishers, New York,1953.

[7] G. Friesecke and B.D. Goddard, *Atomic structure via highly charged ions and their exact quantum states*, Phys. Rev. A 81 (2010) 032516.

[8] D. Gilbarg and N.S. Trudinger, *Elliptic partial differential equations of second order, 2nd edition*, Springer, Berlin, 1983.

[9] S. Goedecker, M. Teter and J. Hutter, *Separable dual-space Gaussian pseudopotential*, Phys. Rev. B 54 (1996) 1703–1710.

[10] D. Gontier, *Existence of minimizers for Kohn-Sham within the Local Spin Density Approximation*, Nonlinearity 28 (2015) 57-76 .

[11] X. Gonze, R. Stumpf and M. Scheffler, *Analysis of separable potentials*, Phy. Rev. B 44 (1991) 8503–8513.

[12] L. Grafakos and G. Teschl, *On Fourier transforms of radial functions and distributions*, J. Fourier Anal. Appl. 19 (2013) 167–179.

[13] H. Hellmann, *A new approximation method in the problem of many electrons*, J. Chem. Phys. 3 (1935) 61.

[14] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, *"Schrödinger inequalities" and asymptotic behavior of the electron density of atoms and molecules*, Phys. Rev. A 16 (1977) 1782–1785.

[15] E.L. Ince, *Ordinary Differential Equations*, Dover, New York, 1944.

[16] G.P. Kerker, *Non-singular atomic pseudopotentials for solid state applications*, J. Phys. C: Solid St. Phys., 13 (1980) L189–L194.

[17] L. Kleinman and D. M. Bylander, *Efficacious form for model pseudopotentials*, Phys. Rev. Lett. 48 (1982) 1425–1428.

[18] W. Kohn and L.J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev. 140 (1965) A1133–A1138.

[19] J.-L. Lions and J. Peetre, *Sur une classe d'espaces d'interpolation*, Inst. Hautes Etudes Sci. Publ. Math. 19 (1964) 5–68.

[20] R.M. Martin, *Electronic Structure Basic Theory and Practical Methods*, Cambridge University Press, 2004.

[21] M. Reed and B. Simon, *Methods of modern mathematical physics, Vol. IV: Analysis of operators*, Academic Press, New York, 1978.

[22] B. Simon, *Trace ideals and their applications*, Mathematical Surveys and Monographs, American Mathematical Society, 2005.

[23] J. Sokolowski and J.-P. Zolésio, *Introduction to shape optimization*, Springer Series in Computational Mathematics, Vol. 16, Springer-Verlag, Berlin, 1992.

[24] J.P. Solovej, *Proof of the ionization conjecture in a reduced Hartree-Fock model*, Invent. Math. 104 (1991) 291–311.

[25] G. Stampacchia, *Le problème de Dirichlet pour les équations elliptique du second ordre à coefficients discontinus*, Ann. Inst. Fourier 15 (1965) 189–258.

[26] J. R. Trail and R.J. Needs, *Norm-conserving Hartee-Fock pseudopotentials and their asymptotic behavior*, J. Chem. Phys. 122 (2005) 014112.

[27] N. Troullier and J.L. Martins, *Efficient pseudopotentials for plane-wave calculations*, Phys. Rev. B 43 (1991) 1993–2006.

[28] D. Vanderbilt, *Soft self-consistent pseudopotentials in a generalized eigenvalue formalism*, Phys. Rev. B 41 (1990) 7892–7895.

[29] E.T. Whittaker and G.N. Watson, *A course of modern analysis*, Cambridge University Press, 1963.

[30] M.A. Wieczorek and F.J. Simons, *Localized spectral analysis on the sphere*, Geophys. J. Int. 162 (2005) 655-675.